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## COMMUNICATION

## Room-temperature method for coating ZnS shell on semiconductor quantum dots

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**A green room-temperature method based on phase transfer and a reaction between Zn<sup>2+</sup> and S<sup>2-</sup> in toluene for coating ZnS shell on CdSe and Ag<sub>2</sub>S quantum dots (QDs), respectively, has been developed. In this method, the S<sup>2-</sup> anions in Na<sub>2</sub>S aqueous solution were transferred to toluene via electrostatic interactions between the anions and didodecyldimethylammonium bromide (DDAB), which served as an excellent sulfur precursor and thereby reacted with Zn<sup>2+</sup> to form ZnS shell on the surface of semiconductor QDs in the presence of QDs in organic phase. After ZnS shell was coated on QDs, the photoluminescence (PL) intensities of the CdSe and Ag<sub>2</sub>S QDs were found to increase approximately 12 times and 14 times, respectively, while both the emission wavelengths and the peak shape were well maintained. The proposed method is novel, simple and robust, providing a green solution to the preparation of ZnS shell-coated QDs.**

Semiconductor nanocrystals (quantum dots, QDs) exhibit bright size-dependent band gap emissions, making QDs ideal inorganic materials for solar cells and biomedical labeling,<sup>1-3</sup> especially for in vivo imaging. Furthermore, in recent years, near-infrared (NIR) fluorescent QDs attract great interest due to the large penetration depth of NIR fluorescence and low auto-fluorescence emitted from tissues (or cells) in NIR region,<sup>4,5</sup> and many kinds of Cd-free and Pb-free NIR QDs have been successfully synthesized.<sup>6-12</sup> However, the low quantum yield of NIR QDs restricts their further development in biomedical labeling. The quantum yield of QDs is always affected by the surface defect states and environmental factors (such as oxygen, pH, etc.).<sup>13,14</sup> Coating an insulating inorganic shell with a wider band gap on QDs is an effective approach to passivating the surface defect states and

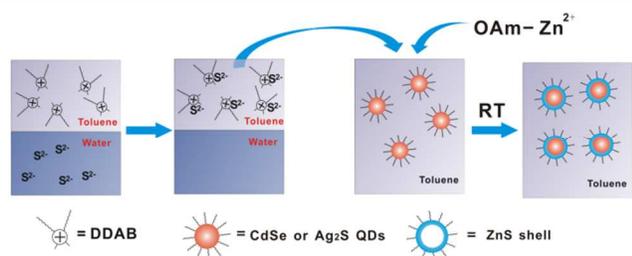
preventing the influence of environmental factors, thus increasing the quantum yield and stability of fluorescence.<sup>3,15,16</sup>

ZnS is the most studied shell material for core/shell QDs due to its wide band gap and low cytotoxicity, and has been successfully applied to enhance the fluorescence of many kinds of QDs, such as CdSe/ZnS and CuInS<sub>2</sub>/ZnS core/shell QDs.<sup>11,17,18</sup> However, the previous methods for coating ZnS shell on QDs were performed under harsh reaction conditions (high temperature or tedious oxygen-free process). Meanwhile, the high reaction temperature always results in the undesired changes in optical properties of the core (such as redshift of emissions), which is unfavorable for synthesizing high quality QDs with controllable optical properties. Therefore, it is necessary to develop a green method for coating ZnS shell on QDs at room temperature (RT).

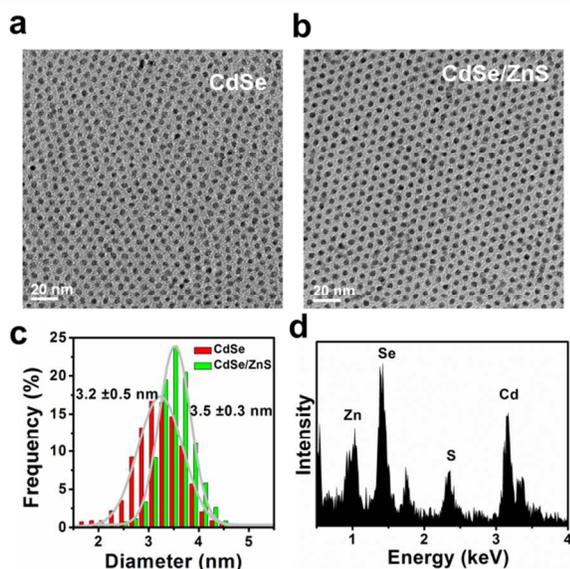
In fact, the reaction between Zn<sup>2+</sup> and S<sup>2-</sup> in aqueous solution could easily occur to get ZnS precipitate at room temperature. However, most of high quality QDs core are synthesized in organic phase.<sup>11,19-23</sup> In this work, a room-temperature method capable of preparing the ZnS shell-coated QDs via S<sup>2-</sup> phase transfer and the growth of ZnS shell on QDs in organic phase is described. The synthetic procedure for preparation of ZnS shell-coated QDs is shown in Fig. 1. The S<sup>2-</sup> anions in Na<sub>2</sub>S aqueous solution are transferred to organic phase (toluene) from water phase via the electrostatic interaction between the S<sup>2-</sup> anions and didodecyldimethylammonium bromide (DDAB) to get DDAB-S<sup>2-</sup> precursor, which is similar with the reported phase transfer process of gold ions.<sup>24</sup> Such DDAB-S<sup>2-</sup> precursor shows high reactivity with Zn<sup>2+</sup> (Zn-oleylamine complex, OAm-Zn<sup>2+</sup>) in toluene at room temperature, because the actual reaction between DDAB-S<sup>2-</sup> and OAm-Zn<sup>2+</sup> is the reaction between S<sup>2-</sup> and Zn<sup>2+</sup>. Similar reaction of (NH<sub>4</sub>)<sub>2</sub>S and Cd(OA)<sub>2</sub> in octadecene (ODE) also exhibits high reactivity and has been applied to produce CdS QDs at room temperature.<sup>25</sup> Moreover, oxygen-free process is not needed in

our method because the core QDs and the reagent used in this method are air-stable at RT.

It is worthwhile to note that, the reaction of DDAB-S<sup>2-</sup> with OAm-Zn<sup>2+</sup> does not require complicated redox reactions, while they are always involved in conventional synthesis method.<sup>26</sup> Based on this reaction, a green RT method for coating ZnS shell on QDs has been successfully applied to coat ZnS shell on CdSe and Ag<sub>2</sub>S QDs, respectively. To our knowledge, there is no report on successfully coating ZnS shell on Ag<sub>2</sub>S QDs. After ZnS shell is coated on QDs at RT without oxygen-free process, the quantum yield of CdSe and Ag<sub>2</sub>S QDs obviously increases. It's exciting that both the emission wavelength and the peak shape maintain as before. This method simplifies the synthesis conditions and provides a general protocol for synthesizing other core/shell nanocrystals under mild conditions.



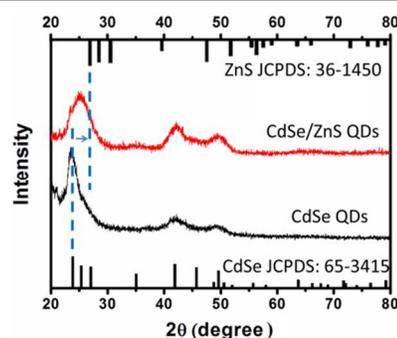
**Fig. 1** Schematic illustrations of a novel method of preparing ZnS shell-coated QDs at room temperature.



**Fig. 2** TEM images of CdSe core (a) and CdSe/ZnS core/shell QDs (b), and the corresponding size distribution histograms (c); EDX spectrum of the CdSe/ZnS core/shell QDs (d).

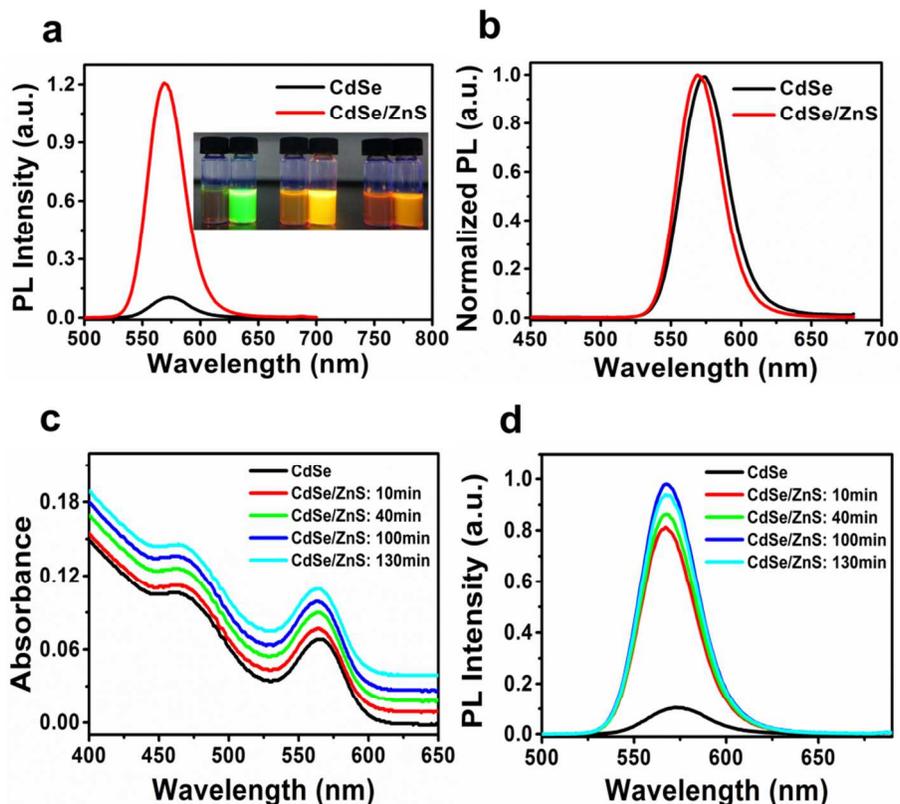
TEM images show that the CdSe core and CdSe/ZnS core/shell QDs are well monodisperse with narrow size distribution (Fig. 2a, b). The size distribution histograms (Fig. 2c) show that the size of CdSe QDs were increased from  $3.2 \pm 0.5$  nm to  $3.5 \pm 0.3$  nm after ZnS shell was coated on QDs and the size distribution was well improved. It is interesting that the increase of size did not result in redshift of fluorescence emission (will be discussed below), implying that the size of CdSe core was maintained and the increase of size attributed to the

growth of ZnS shell on the CdSe core QDs. This conclusion is further confirmed by the signal of elements Zn and S in the energy-dispersive X-ray (EDX) analysis of the as-prepared CdSe/ZnS core/shell QDs (Fig. 2d). Powder X-ray diffraction (XRD) (Fig. 3) results show that the positions and relative intensities of all diffraction peaks of CdSe core match well with those of hexagonal CdSe (JCPDS Card No. 65-3415), but the peak of the as-prepared CdSe/ZnS core/shell QDs appears a short shift to that of ZnS crystal (JCPDS Card No. 36-1450). This phenomenon is in good agreement with the reported CdSe/CdS core/shell nanocrystals,<sup>27,28</sup> suggesting the successful formation of CdSe/ZnS core/shell nanocrystals. Thus, it could be concluded that the ZnS shell has successfully been grown on the CdSe QDs through our RT method without oxygen-free process.



**Fig. 3** XRD patterns of CdSe core and CdSe/ZnS core/shell QDs.

As ideal inorganic fluorophores, the fluorescence of QDs is the most concerned properties. Fig. 4a shows the photoluminescence (PL) spectra of CdSe core and CdSe/ZnS core/shell QDs of same concentration. It's obvious that the PL intensity of the CdSe QDs was significantly increased approximately 12 times after ZnS shell-coating, according to the fluorescence photographs (Fig. 4a, inset), suggesting that the RT method is effective for coating ZnS shell to improve the fluorescence of CdSe QDs. The PL quantum yield (QY) of the CdSe/ZnS core/shell QDs increased to 40% (using Rhodamine 6G as a reference standard, QY=95% in Ethanol). Moreover, it is noteworthy that the emission wavelength and the peak shape were well maintained after ZnS shell-coating, as shown in the normalized PL spectra of CdSe and CdSe/ZnS QDs (Fig. 4b). The full width at half maximum (FWHM) of the PL spectra appears a negligible change from 37 nm to 36 nm and the emission wavelength shows a slight blue-shift only about 2 nm after ZnS shell-coating. The slight blue-shift may attribute to cation exchange on the surface of QDs, it's possible that Zn<sup>2+</sup> ions replace the Cd<sup>2+</sup> near the surface, slightly decreasing the core size.<sup>29</sup> Therefore, the actual ZnS shell thickness may be a little thicker than the measured size increase (approximately 0.3 nm) between CdSe and CdSe/ZnS. The XRD result of CdSe/ZnS QDs (Fig. 3) matches with the XRD pattern of ZnS coated CdSe with coverage of 1.3 monolayer (approximately 0.4 nm) reported by Bawendi's group.<sup>17</sup> By contrast, the emission and absorption peaks show obvious undesired red-shift (about 24 nm and 19 nm), respectively, in the conventional high temperature method for coating ZnS shell on CdSe QDs (Fig. S1 in the ESI†). Therefore, compared with the high temperature method, room-temperature growth of ZnS shell is more beneficial to maintaining the intrinsic properties of core QDs (emission wavelength and emission peak shape).

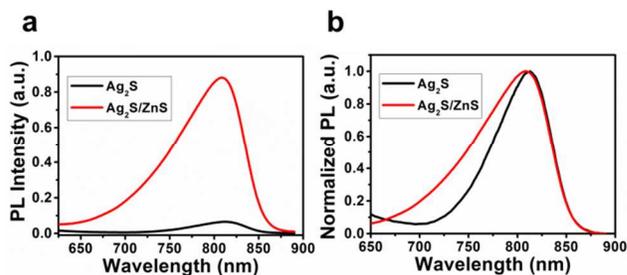


**Fig. 4** PL spectra (a) and the normalized PL spectra (b) of CdSe core and CdSe/ZnS core/shell QDs of same concentration. The fluorescence photographs (a, inset) of several CdSe samples and the corresponding CdSe/ZnS core/shell QDs samples. Temporal evolution of absorption spectra (c) and PL spectra (d) of CdSe/ZnS core/shell QDs coating at room-temperature.

The temporal evolution of absorption spectra and PL spectra of the growth of ZnS shell on CdSe QDs are shown in Fig. 4c,d. The PL intensities were increased with the growth time, and reached a maximum at 100 min and then dropped down. The shapes of absorption and PL spectra of CdSe/ZnS QDs match well with those of the CdSe QDs during the whole growth process of ZnS shell.

Except for CdSe, the RT method was also applied to grow ZnS shell on Ag<sub>2</sub>S QDs. Ag<sub>2</sub>S QDs have been regarded as ideal QDs for biomedical imaging due to their excellent NIR fluorescence and negligible toxicity,<sup>30,31</sup> and several reports on Ag<sub>2</sub>S QDs have been published.<sup>7,10,32</sup> In our previous work, we reported the synthesis of emission-tunable NIR Ag<sub>2</sub>S QDs,<sup>8</sup> however, the quantum yield of the Ag<sub>2</sub>S QDs was found to be very low. Thus, we chose such Ag<sub>2</sub>S QDs as core to grow ZnS shell to evaluate how the RT method works on the Ag<sub>2</sub>S QDs. To our knowledge, there is no report on successfully coating ZnS shell on Ag<sub>2</sub>S QDs yet. It's exciting that the PL intensity of the Ag<sub>2</sub>S QDs was increased approximately 14 times after the growth of ZnS shell (Fig. 5). The change of the emission wavelength is similar with the case of CdSe QDs, and a slight blue-shift about 2 nm in the Ag<sub>2</sub>S/ZnS core/shell QDs appeared (Fig. 5b). The TEM images (Fig. S2 in the ESI†) show that after the growth of ZnS shell, the size of Ag<sub>2</sub>S QDs was increased from 1.6 nm to 3.5 nm, and the EDX result (Fig. S3 in the ESI†) confirms the presence of Zn element in Ag<sub>2</sub>S/ZnS core/shell QDs. The XRD peak of the Ag<sub>2</sub>S/ZnS core/shell QDs also

shows a short shift to that of ZnS crystal (Fig. S4 in the ESI†), which is similar with the case of CdSe/ZnS core/shell nanocrystals as mentioned above. Thus, it could be concluded that the RT method is also effective to improve the PL intensity of Ag<sub>2</sub>S QDs by coating ZnS shell. In this work, the quality of the CdSe core is better than Ag<sub>2</sub>S core. For instance, the CdSe is determined to have a narrower deviation than that of Ag<sub>2</sub>S (Fig. 2c and Fig. S2c in the ESI†). This may be the reason why the CdSe QDs shows better performance than Ag<sub>2</sub>S QDs in this method.



**Fig. 5** PL spectra (a) and the normalized PL spectra (b) of Ag<sub>2</sub>S core and Ag<sub>2</sub>S/ZnS core/shell QDs of same concentration.

In summary, we developed a green RT method for coating ZnS shell on CdSe and Ag<sub>2</sub>S QDs, respectively, without using harsh reaction conditions. In particular, we demonstrated the first example of

preparing ZnS-coated Ag<sub>2</sub>S QDs by using the RT method. The results show that the PL intensities of the ZnS shell-coated CdSe and Ag<sub>2</sub>S QDs were greatly increased up to approximately 12 times and 14 times, respectively, while the emission wavelength and the peak shape (FWHM) were well maintained. Our novel protocol simplifies the synthesis conditions (conventionally, high temperature methods) for synthesis of core/shell nanocrystals and provides an opportunity to develop a generalized green method for synthesizing metal sulfide nanoparticles.

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### Notes and references

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## Table of Contents

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