Facile synthesis and characterization of highly luminescent UV-blue-emitting ZnSe/ZnS quantum dots via a one-step hydrothermal method†

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The synthesis of water-soluble blue-emitting quantum dots (QDs) in aqueous solutions has attracted much attention recently, and here we report the synthesis of high-quality core/shell ZnSe/ZnS QDs through a one-step hydrothermal route with thiol ligand N-acetyl-L-cysteine (NAC) as the stabilizer. The impacts of various synthesis factors on the fluorescence properties of the prepared QDs have been systematically investigated. Under optimal conditions, the as-prepared QDs exhibit high photoluminescence quantum yield (~39%), narrow full-width at half-maximum, and high photostability, due to the formation of a protective ZnS shell on the ZnSe core through the decomposition of NAC under high temperature. The core/shell structure of the ZnSe/ZnS QDs was verified by UV irradiation experiment, X-ray powder diffraction, and electron diffraction spectroscopy.

1. Introduction

High-quality quantum dots (QDs) are of great interest and have been widely investigated due to their unique size-dependent properties.1–3 Over the past two decades, great efforts have been put forward for the synthesis of green to near infrared emitting II–VI semiconductor QDs (500–750 nm).4–7 With their bulk band gap at ~2.7 eV (460 nm),8 ZnSe QDs are usually considered as the ideal candidate UV-blue-emitting nanomaterials for optoelectronic devices9 and biomedical imaging because of its low toxicity compared with other wide-band gap materials for optoelectronic devices10 and e9 material around the QDs, has been proven as a key procedure to improve the fluorescence efficiency and stability of prepared nanocrystals.11 Zhu et al. have synthesized ZnSe/ZnS core/shell nanostructures through two-step route, and the QY of prepared QDs reached 65%.12 Yet, after the preparation of GSH-capped ZnSe core QDs for 60 minutes, mixture solution containing Zn(OAc)2, GSH and thiourea need to be added to the as-prepared ZnSe core QDs crude reaction solution to form ZnS shell. It is time-consuming and not convenient for synthesis. Some literatures16,17 have reported the enhanced luminescent qualities of prepared ZnSe QDs through the optical irradiation to form core/shell structure on the surface of QDs. Shavel et al. have improved the QY of prepared ZnSe QDs up to 25–30% through this method.17 However, these synthesis methods require complicated procedure and long reaction time, and its enhancement in QY was limited. Dong et al. have proposed a facile, two-step method to synthesize ZnSe/ZnS core/shell QDs under mild conditions (low temperature < 150 °C), but this synthesis process must include the transformation of oil-soluble ZnSe QDs into water-soluble ones through changing the original ligands (oleic acid) with 3-mercaptoacryionic acid (MPA) before the growth of ZnS shell, which is a complicated process.18 Recently, new methods have been employed to prepare high-quality QDs. Ren presented a new aqueous procedure for rapid preparation of high quality ZnSe/ZnS...
alloyed QDs with QY up to 17% through the use of microwave irradiation, but the synthesis procedure requires professional microwave equipment and the prepared QDs possess strong trap emission at 480 nm. As a method to direct synthesize QDs in aqueous phase, the hydrothermal method inherits all the merits of aqueous methods, and overcomes the problem of surface defects caused by low temperature and long interaction time in refluxing route (the reaction temperature cannot exceed 100 °C). The high reaction temperature in this method greatly shortens the preparation cycle, and can significantly improve the surface quality of prepared QDs. However, the synthesis of ZnSe/ZnS QDs through hydrothermal route has not been reported in the published literature. The choice of stabilizer is of great importance for the synthesis of core/shell QDs through hydrothermal route. Zhong has adopted a mixture of L-glutathione (GSH) and MPA as stabilizers, and successfully synthesized high quality ZnSe/ZnS QDs. The synthesis process, however, was complex and time-consuming. In our study, the high-quality ZnSe/ZnS QDs have been synthesized through one-pot hydrothermal route by using NAC as the stabilizer. The synthesis procedure requires no further treatment and the prepared ZnSe/ZnS QDs possess good stability and excellent QY (up to 39%). Compared to traditional thiols (such as thioglycerol, thioglycolic acid, 3-mercaptopropionic acid, e.g.), the thiol ligand NAC is known as an antioxidant and impurity removal reagent, and can be used to protect cells from oxidation and QDs-induced cytotoxicity. The experimental results show that the employment of single stabilizer NAC works both as the stabilizer and sulfur ions provider under high temperature and high pressure in the hydrothermal method to synthesize high-quality ZnSe/ZnS QDs with core/shell structure. The as-prepared QD exhibited excellent water-solubility, stability and high QY, and their structure has been verified by post-illumination experiment, X-ray powder diffraction (XRD), and electron diffraction spectroscopy (EDS).

2. Materials and methods

2.1. Materials

NAC was purchased from Sigma. Selenium (reagent powder), ZnCl₂, sodium borohydride, sodium hydroxide, isopropyl alcohol were obtained from Sinopharm Chemical Reagent and were used as received without additional purification. High purity argon was from Sichuan Tianyi Science & Technology Co. Ltd. All solutions were prepared using Milli-Q water as the solvent.

2.2. Synthesis of ZnSe/ZnS QDs

NaBH₄ was used to react with Selenium at a molar ratio of 4:1 in 3 mL DI water to prepare sodium hydroselenide (NaHSe). The freshly prepared NaHSe solution was kept in the fridge for further use. ZnCl₂ (0.16 M, 1 mL) and NAC were dissolved in 50 mL of DI water under vigorous stirring for 30 min. The precursor solution was adjusted to pH 9.0–10.5 by stepwise addition of NaOH. The prepared precursor solution was deaerated with high purity Ar for 20 min in an ice-water bath under vigorous stirring. Subsequently, the NaHSe solution at 0 °C was added to the solution under vigorous stirring for 3 min. The molar ratio of Zn:Se was fixed at 1.0:0.04–0.125 and the molar ratio of Zn:NAC was fixed at 1.0:2.4–4.0. Finally, the solution was loaded into a 50 mL Teflon-lined stainless steel autoclave and incubated in an oven at 170–210 °C for a specified period (40–80 min). Afterward, the autoclave was cooled to room temperature by a hydro-cooling process.

ZnSe/ZnS QDs were firstly precipitated by centrifuging a mixture of 2-propanol, a few drops of saturate NaOH and a solution of ZnSe/ZnS QDs at 4000 rpm for 15 min. The as-prepared product was dried overnight under vacuum at 50 °C for further experiments.

2.3. Characterization

UV-visible absorption spectra were acquired with a lambda-35 UV-visible spectrophotometer. Fluorescence spectra were recorded on a LS-55 luminescence spectrometer. XPS measurements were acquired with a VG Multilab 2000 X-ray photoelectron spectrometer. TEM sample was prepared by dropping an aqueous ZnSe/ZnS QDs solution onto Agar carbon-coated copper grids (400 meshes) with the excess solvent evaporated. TEM image was obtained with an FEI Tecnai G220 Twin transmission electron microscope. XRD spectra were recorded on a D8-advance X-ray diffraction. EDS spectra were captured using an FEI Quanta 200 scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The QY of ZnSe/ZnS QDs was measured according to literature, quinolone sulfate was chosen as the reference standard (QY = 54.6%). All optical measurements were performed at room temperature under ambient conditions.

3. Results and discussion

3.1. The optimization of synthesis conditions of NAC capped ZnSe/ZnS QDs

Due to their high surface-to-volume ratio of QDs, the luminescent qualities of prepared QDs are largely determined by their surface structure, which in turn is greatly influenced by pH, reaction temperature, molar ratio of reactants and reaction time during synthesis procedure. Thus, the optimum synthesis environment is of great importance to obtain high-quality ZnSe/ZnS QDs.

3.1.1. Effect of the reaction temperature. The optimum reaction temperature was investigated when other reaction factors were fixed (Zn²⁺:HSe⁻ : NAC = 1.0 : 0.05 : 3.6, pH = 9.7, 60 min, [Zn²⁺] = 3.2 mmol L⁻¹). As shown in Fig. S1, the QY of as-prepared QDs reached maximum when the reaction temperature was 200 °C. Compared to the low reaction temperature in traditional refluxing route (<100 °C), the high temperature in hydrothermal route provides better environment for fast growth rate of nanocrystals, rendering less surface defects, less nonradioactive transitions and thus improved spectra properties of as-prepared QDs. Compared with other methods, the relative intensity of defect peak obviously decreases (Fig. 1). Furthermore, the increase of reaction
temperature led to a red shift of their emission maxima ($\lambda_{em}$) (from 390 nm to 420 nm) (Fig. S2†), showing that the diameter of as-prepared QDs increased with the reaction temperature.

When the reaction temperature is too low (<170 °C), the low growth rate of QDs would lead to low QY, and fails to exhibit the merits of hydrothermal route. However, the comparatively-high temperature (>200 °C) also resulted in lower QY because it deters the stabilizer NAC from combining onto the surface of QDs. When the reaction temperature reaches as high as 230 °C, precipitation occurred in the autoclave with a pungent smell, showing that the stabilizer NAC began to decomposition under high temperature, losing its function as stabilizer.

3.1.2. Effect of the reaction time. Reaction time also plays an important role in QY of as-prepared QDs. By controlling the reaction time (40–80 min) in the same reaction condition (Zn$^{2+}$ : HSe$^{-}$ : NAC = 1.0 : 0.05 : 3.6, pH = 9.7, 200 °C, [Zn$^{2+}$] = 3.2 mmol L$^{-1}$), the QY of as-prepared QDs reached maximum at 60 min (Fig. S3†). At the initial stage of the reaction, NAC worked only as stabilizer to facilitate the combination of Zn$^{2+}$ and HSe$^{-}$ to form ZnSe QDs. The shorter reaction time led to smaller QDs diameter and lower QY due to more surface defects caused by high surface-to-volume ratio. After this fast growing period, the stabilizer NAC started thermal decomposition process and released reactive S atoms, triggering the formation of ZnS shell on the surface of ZnSe core. The formation of shell increased the diameter of as-prepared QDs, leading to red-shift of luminescent peak (Fig. S4†). Longer reaction time (>80 min) would cause the excessive decomposition of NAC, depriving its ability as stabilizer and thus causing precipitation in the solution (Fig. 2).

3.1.3. Effect of the pH of the precursor solution. By controlling the pH value of the precursor solution (9–10.5) in the same reaction condition (Zn$^{2+}$ : HSe$^{-}$ : NAC = 1.0 : 0.05 : 3.6, 60 min, 200 °C, [Zn$^{2+}$] = 3.2 mmol L$^{-1}$), the QY of as-prepared QDs reached maximum at pH 9.7 (Fig. S5†), showing that the weakly alkaline reaction environment is profitable for the formation of high-quality QDs. The corresponding PL spectra of these QDs were shown in Fig. 3. In acidic environment, the protonation of the thiol moiety of NAC discourages its combination with Zn$^{2+}$; in strongly alkaline solution, on the other hand, the excessive hydroxyl ions would compete with NAC for the combination opportunity of Zn$^{2+}$, impeding the formation of NAC-capped QDs.

3.1.4. Effect of the molar ratio of reactants. The molar ratio of reactants would determine the structure of as-prepared QDs, and further influence their luminescent properties. To investigate optimum molar ratio, the molar ratio of NAC/Zn$^{2+}$ was first set as a constant (NAC : Zn$^{2+}$ = 3.6 : 1.0) to get the best molar ratio of HSe$^{-}$/Zn$^{2+}$. As shown in Fig. 4 and S6† the best molar ratio is 0.05. The explanation might be analogous to that of CdTe QDs. The enhancement of the HSe$^{-}$/Zn$^{2+}$ ratio led to a higher Se content in as-prepared QDs, and thus low QY, because of the nonradioactive combination pathways caused by the existence of dangling bonds of Se ions on the surface of QDs and the easy proneness of oxidation.

Then the molar ratio of HSe$^{-}$/Zn$^{2+}$ was fixed at 0.05, and the optimum molar ratio of NAC/Zn$^{2+}$ was investigated in the range of 1.2–4.0 (Fig. 5). When the molar ratio was at 1.2, the
precursor solution was turbid, because Zn$^{2+}$ ions could not form stable zinc thiol complexes without adequate NAC. The experiments showed that proper molar ratio (NAC : Zn$^{2+}$ = 3.6 : 1.0) was favourable to the formation of NAC-rich QDs surface (Fig. S7†). NAC, first of all, served as stabilizer to ensure the water-solubility of as-prepared QDs and decrease the trap site on the surface of QDs; meanwhile, it served as an excellent sulfur provider for the formation of metal sulfide QDs in aqueous synthesis, because of its gradual decomposition at high-temperature in alkaline media, steadily supplying sulfur ions to form ZnS shell on the surface of ZnSe QDs.40,41 However, when the concentration of NAC further increased, the Zn$^{2+}$ ions were capped by excessive NAC, interfering their reaction with HSe$^-$/C0 to form ZnSe core and thus weakening the fluorescence intensity of as-prepared QDs.

Through a series of experiments motioned above, we discovered that the QYSs of prepared QDs can be greatly influenced by reaction temperature, reaction time, pH value of precursor and reactant ratios, but only the reaction time and temperature can exhibit obvious impacts on the emission peak of prepared QDs. The optimum reaction conditions have emerged: molar ratio of Zn$^{2+}$ : HSe$^-$/C0 : NAC is 1.0 : 0.05 : 3.6, pH is 9.7, reaction time is 60 min and reaction temperature is 200 °C. The PL and UV spectra of as-synthesized ZnSe/ZnS QDs under optimum condition are shown in Fig. 6. As shown in the inset of Fig. 6, the as-prepared ZnSe/ZnS QDs are colourless and transparent under visible light and show strong blue fluorescence under the UV light (365 nm). By choosing quinine sulfate as the reference standard (QY = 54.6%), the QY of ZnSe/ZnS QDs is 39.30% as measured according to the literature.32 The detailed process of QYSs calculation is provided in ESI.† All the samples showed a sharp well-resolved first excitonic absorption, indicating a narrow size distribution and high crystallinity of the obtained samples. We have investigated the effect of pH on the emission intensity of NAC-capped ZnSe/ZnS QDs. As shown in Fig. S8,† the prepared ZnSe/ZnS QDs exhibits weak fluorescence intensity in acidic solution, and shows significantly better performance in neutral or alkaline solutions. Since the ligand NAC on the surface of QDs is Lewis base, it will theoretically be protonated and detached from QDs in acidic solution; then the naked QDs possess worse stability and more surface defects, and exhibit lower PL intensity. By contrast, the better performance of ZnSe/ZnS QDs in neutral and alkaline solutions ensure the practicability as biosensor and boilable in actual biochemical environments.

3.2. Characterization and study on the growth mechanism of ZnSe/ZnS QDs

3.2.1. Photostability. We regard the improvement in optical quality of the prepared UV-blue emitting QDs as the result of decrease of surface defects on QDs caused by the rapid growth rate under high reaction temperature (200 °C), and, most importantly, the result of core/shell structure of ZnSe/ZnS QDs. Fig. 7 schematically shows the growth mechanism of ZnSe/ZnS QDs. At the initial stage, NAC only work as a stabilizer to facilitate the combination of Zn$^{2+}$ and HSe$^-$/C0 to form ZnSe QDs. As the reaction time prolongs, the capping NAC ligand starts to undergo thermal decomposition to release reactive S atom to form ZnS shell on the surface of the ZnSe core. ZnS represents a nearly ideal candidate for the

Fig. 4 PL spectra of NAC-capped ZnSe/ZnS QDs prepared at different HSe$^-$/Zn$^{2+}$ values.

Fig. 5 PL spectra of NAC-capped ZnSe/ZnS QDs prepared at different NAC/Zn$^{2+}$ values.

Fig. 6 PL spectrum and UV-visible absorption spectrum of NAC-capped ZnSe/ZnS QDs. The insets are images of as-prepared ZnSe/ZnS QDs illuminated under visible light (left) and UV light (right).
construction of core/shell structures around the ZnSe core due to its high bandgap (3.5 eV) and small lattice parameter mismatch (4.5%) with respect to ZnS. Like the well-known CdSe/ZnS and CdSe/CdS core/shell structures, the wider band gap material ZnS depositing around the narrower band gap material ZnSe forms a type-I core/shell structure. The valence-band offset between ZnSe and ZnS is about 0.58 eV while there is hardly any conduction-band offset (0.03 eV) between ZnSe and ZnS. Therefore, in the ZnSe/ZnS core/shell structure, the hole will remain preferentially localized in the ZnSe core. Moreover, the ZnS shell also reduced the vacancies and trap sites on the core surface, which contributed to the enhancement of the PL emission. With a prolonged heating time (40–60 min), the formed ZnS shell gradually thickens, and the nanocrystals grow to larger size. The QYs of the resulting core/shell QDs increase steadily up to 39.3% and an obvious red shift could be seen in the absorption and PL spectra due to partial leakage of the exciton into the ZnS shell. The prepared QDs has been characterized and their core/shell structure of has been testified through UV radiation experiments, XRD, TEM, EDS and XPS.

A series of experiments have been carried out to testify the photostability of QDs prepared at different reaction times. The solutions with the nanocrystals in ambient conditions were continuously irradiated by a 16 W xenon lamp at 365 nm and their emission intensities were monitored over a period of 100 min. As shown in Fig. 8, the strongest PL intensities of samples after treatment are 6.0 times and 1.2 times higher than the original intensity corresponding to QDs prepared at 40 min and 60 min respectively.

For ZnSe/ZnS QDs prepared at 40 min, the ZnS shell formed on the surface of ZnSe core is too thin to effectively reduce the surface defects of QDs. When under the irradiation of UV light, the stabilizer NAC in the solution releases S atoms due to photodecomposition effect, and these S atoms cap on the surface of QDs, increase the thickness of ZnS shell, smooth the original core surface and passivate surface radiative recombination sites, which brings forward the increase of PL QYs. However, since the surface change of this process is still limited, the QY of ZnSe/ZnS QDs prepared at 40 min after the irradiation still remains low (~10%). On the other hand, for the QDs prepared at 60 min, the long reaction time ensures thick ZnS shell on the surface of ZnSe core, protecting it from the impact of UV radiation. The excellent photostability of prepared QDs is beneficial to their applications in biochemical detections and cell imaging.

3.2.2. XRD and TEM. Fig. 9 shows the power XRD patterns of QDs prepared at different reaction times (40 and 60 min). The diffraction peaks are located between the cubic ZnSe (JCPDS no. 80-0021) and ZnS phase (JCPDS no. 80-0020). The diffraction peaks of the as-prepared QDs exhibit obvious shift from cubic ZnSe to cubic ZnS phase because of the smaller lattice parameters of ZnS, and their extremely close approach to the peaks of cubic ZnS shows the effective capping of ZnS onto ZnSe core. The as-prepared nanocrystals belong to cubic structure (zinc blende). The similar diffraction peaks of QDs prepared at 40 min and 60 min prove that both of them are ZnSe/ZnS QDs. The morphology of the ZnSe/ZnS QDs was studied by TEM (Fig. 10). It demonstrates high-quality of non-aggregated spherical particles of these nanoparticles with an average size of 3.4 nm.

3.2.3. EDS. The EDS technique has been employed to probe a semi-quantitative picture of the composition of the NAC-capped ZnSe/ZnS QDs. The growth of ZnS shell around the ZnSe cores was also clearly demonstrated by the EDS measurements (Fig. 11). The EDS spectra reveal the existence of Zn, S, and Se in the sample, implying that the nanocrystals perhaps possess a core/shell structure of ZnSe/ZnS. With a prolonged heating time, the corresponding values of [S]/([Se] + [S]) increased gradually. The [S]/([Se] + [S]) molar ratios in the samples increased from 45.4% corresponding to the prepared QDs at 40 min to 80.1% corresponding to the obtained QDs at

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**Fig. 7** Schematic illustration of the synthesis of water-soluble ZnSe/ZnS core/shell QDs.

**Fig. 8** Photostability of NAC-capped QDs prepared at different reaction times of (a) 40 min and (b) 60 min.

**Fig. 9** XRD pattern of NAC-capped ZnSe/ZnS QDs prepared at 40 and 60 min at 200 °C. The lines in spectra showed standard diffraction lines of cubic ZnSe (down) and ZnS (up).
60 min. With a prolonged heating time, the QDs grew to larger size and the molar ratio of \([S]/([Se] + [S])\) increased obviously, implying the growth of nanocrystals was partially attributed to the increased thickness of ZnS shell on the surface of ZnSe core. Since the sulfur in the initial sample was mainly from the stabilizer NAC and large nanocrystals possess smaller surface area/volume ratio, the molar ratio of \([S]/([Se] + [S])\), theoretically, should decrease with the increase of particle diameter. In our experiments, however, the molar ratio increases with the growth of QDs. We suppose that is the result of the increased thickness of ZnS shell of prepared ZnSe/ZnS QDs with prolonged reaction time.

3.2.4. XPS. XPS is an analytical tool sensitive to the atomic composition of QDs.\(^{18,44}\) It was thus used to analyze the chemical composition of the NAC-capped ZnSe/ZnS QDs (Fig. S9†). The appearance of characteristic Zn (2p\(_{3/2}\)) peaks at 1021 eV and Zn (2p\(_{1/2}\)) peaks at 1044 eV, Se (3d\(_{5/2}\)) peak at 52.8 eV, and S (2p) peak at 161.9 eV are depicted in Fig. 12, indicating the existence of Zn, Se, and S.

4. Conclusions

In summary, we reported the synthesis of core/shell ZnSe/ZnS QDs through one-step hydrothermal route with thiol ligand N-acycetyl-l-cysteine (NAC) as the stabilizer. The impacts of various synthesis factors such as reaction temperature, reaction time, pH of the precursor solution, and molar ratio of reactants on the fluorescence properties of prepared QDs have been systematically investigated. Furthermore, the formation mechanism of the core/shell structure of as-prepared ZnSe/ZnS QDs have been proposed and examined through UV irradiation, XRD and EDS. Under optimal conditions, the as-prepared QDs exhibit high photoluminescence quantum yield (~39%). The high temperature and pressure in hydrothermal route speed up the reaction and reduce the surface defects, rendering excellent fluorescence properties of as-prepared QDs. Besides, the ligand NAC works as the donor of \(S^{2−}\) for the formation of core/shell structure of ZnSe/ZnS QDs.\(^{40,41}\) The as-prepared blue-emitting ZnSe/ZnS QDs will surely have promising applications in the development of optoelectronic devices\(^{47}\) as well as biomedical imaging.\(^{10}\)

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Notes and references


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