



# One-step synthesis of water-soluble ZnSe quantum dots via microwave irradiation

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## ABSTRACT

A facile strategy has been developed for the synthesis of glutathione-capped ZnSe quantum dots (QDs) in aqueous media. The reaction was carried out in air atmosphere with a single step by using  $\text{Na}_2\text{SeO}_3$ , a stable and commercial Se source, to replace the commonly adopted  $\text{NaHSe}$  or  $\text{H}_2\text{Se}$ . Moreover, microwave irradiation improved the photoluminescence quantum yield (PLQY) as well as lowered the trap emission of as-prepared ZnSe QDs. The obtained QDs performed strong band-edge luminescence (PLQY reached 18%), narrow size distribution (full width at half maximum was 26–30 nm) and weak trap emission without post-treatments. The results of transmission electron microscopy and X-ray diffraction demonstrated the small particle size (2–3 nm), good monodispersity and ZnSe(S) alloyed structure of as-prepared QDs. The experimental variables including precursors and stabilizer amounts as well as pH value had significant influence on the PL properties of the ZnSe QDs.

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## 1. Introduction

ZnSe quantum dots (QDs) as wide band gap nanomaterials are excellent UV–blue emitters [1] complementary to those visible and NIR emitting QDs. Due to their low cytotoxicity (without heavy metal ions), ZnSe QDs are potential blue fluorescent biological labels. High quality ZnSe QDs could be achieved via organometallic routes [2,3]. The as-prepared QDs were high luminescent with good monodispersity, while the reaction usually needed elevated temperature and the QDs possessed poor water-solubility due to the hydrophobic surface. In contrast, the aqueous synthesis of ZnSe QDs has attracted more attention in recent years due to the moderate reaction temperature, low-toxicity chemicals and water-soluble products. Yet, the obtained QDs usually suffered from low photoluminescence quantum yield (PLQY) and broad emission [4–6]. To overcome those drawbacks, the post-illumination [7,8], microwave irradiation [9] and biomolecule [10] were employed for the synthesis of strong and narrow band-edge emitting ZnSe QDs. Notably, in most cases, the unstable  $\text{NaHSe}$  or  $\text{H}_2\text{Se}$  were adopted as the Se precursor, thus the synthetic procedure was usually complex and time consuming, considering the pretreatment of Se source and oxygen-free condition.

In this paper, high luminescent and water-soluble ZnSe QDs were synthesized by a facile one-step strategy using microwave irradiation. Here  $\text{NaHSe}$  or  $\text{H}_2\text{Se}$  was replaced by an air-stable and commercial Se source,  $\text{Na}_2\text{SeO}_3$ , which was reduced by  $\text{NaBH}_4$  in ambient conditions to generate  $\text{Se}^{2-}$ . Thus the reaction could be carried out open to air

with a single procedure. The obtained QDs without post-treatments performed a PLQY of 18%, a full width at half maximum (FWHM) of 26–30 nm and weak trap emission. The effects of microwave irradiation and experimental variables on the PL properties of ZnSe QDs were investigated.

## 2. Experimental

In a typical procedure, 148 mg (0.5 mmol) of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 276 mg (0.9 mmol) of glutathione (GSH) were dissolved in 50 ml deionized water and loaded into a 100 ml vessel. Then 9 mg (0.05 mmol) of  $\text{Na}_2\text{SeO}_3$  and excess  $\text{NaBH}_4$  (0.2 g) were added into the above solution with stirring. After several minutes, the pH value of the solution was adjusted to 10.0 by dropwise addition of  $1 \text{ mol l}^{-1}$   $\text{NaOH}$ . The mixture was then refluxed at  $100^\circ\text{C}$  for 60 min under microwave irradiation (300 W). After cooled to room temperature, the QDs were precipitated by 2-propanol and redissolved in deionized water. The procedure was repeated three times then the purified ZnSe QDs were dried under vacuum.

The transmission electron microscopy (TEM) image and selected-area electron diffraction (SAED) pattern were recorded by JEM2010 with an accelerating voltage of 200 kV. The X-ray diffraction (XRD) measurement was performed on Rigaku D/MAX-rA diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The absorption and PL spectra were acquired on Nicolet Evolution 300 UV–vis spectrometer and Perkin-Elmer LS-55 fluorescence spectrometer at 310 nm excitation, respectively. The PLQY of ZnSe QDs was obtained referencing to 2-aminopyridine (PLQY = 60% in 0.1 M  $\text{H}_2\text{SO}_4$  [11]) with the described method [10].

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### 3. Results and discussion

Fig. 1a shows the temporal evolution of absorption and PL spectra of as-prepared ZnSe QDs. The PL spectra were dominated by band-edge emission in the near-ultraviolet region with a FWHM of 26–30 nm. With prolonged heating, both the absorption and emission peaks showed a red-shift, while the trap emission (400–600 nm) decreased steadily and maintained at low intensities. The well-resolved excitonic peak at shorter wavelength gradually became featureless, indicating the homogeneous nucleation of the QDs and broadening of particle size distribution with the crystal growth. The obtained ZnSe QDs exhibited a maximum PLQY of 18% at the emitting wavelength of 376 nm. In this synthesis, microwave irradiation provided a faster growth rate and higher PLQY to ZnSe QDs, contrasted to the conventional heating route (resulting PLQY was 10%). Additionally, the distinct excitonic peak and weak trap emission, revealed in Fig. 1b, implied that the as-prepared QDs had a more narrow size distribution and less surface defects than those prepared by oil-bath heating, probably owing to the homogeneous heating and rapid crystal growth under microwave irradiation [9,12].

The crystallinity and structure of the obtained QDs were demonstrated by the XRD pattern as revealed in Fig. 2a. The QDs belonged to the cubic structure with the diffraction peaks located between those of cubic ZnSe (JCPDS No. 37-1463) and ZnS (JCPDS No. 05-0566), indicating the formation of ZnSe(S) alloyed structure. The sulfur probably came from the decomposition of GSH during the heating process [13,14]. The grain size of the QDs was calculated to be 2.3 nm, using the Scherrer equation with the (111) peak. The TEM image (Fig. 2b) illustrated the nearly spherical and monodispersed

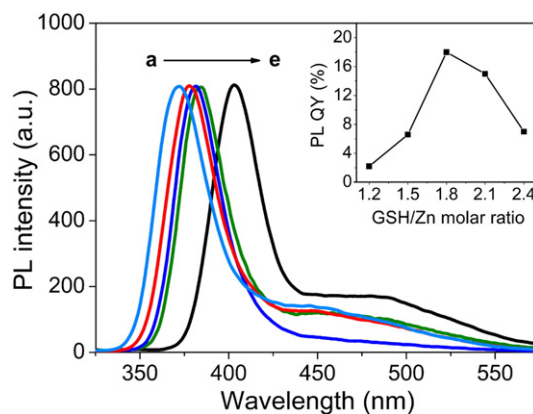


Fig. 3. PL spectra and PLQY (inset) of ZnSe QDs with different GSH/Zn molar ratios. (a) 2.4:1, (b) 2.1:1, (c) 1.8:1, (d) 1.5:1, (e) 1.2:1.

QDs. The particle diameter appeared to be 2–3 nm, in agreement with the calculated value from the XRD result.

To investigate the effect of stabilizer concentration on the PL properties of ZnSe QDs, we varied the GSH/Zn molar ratio from 1.2:1 to 2.4:1 with fixed Zn/Se molar ratio (10:1) and pH value (10.0). With the commonly adopted ratio at 1.2:1, the reaction solution turned white turbid when refluxed at 100 °C. The reason might be the accelerated decomposition of GSH at high temperature in air atmosphere, which leads to insufficient stabilizer to prevent the QDs from aggregation. The deficient passivation to the QD surface caused obvious trap emissions, as shown in Fig. 3. While with high

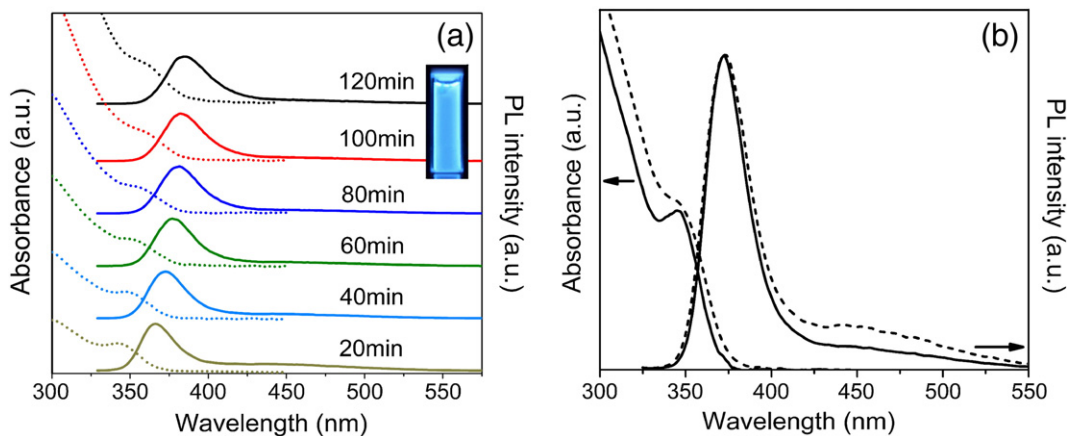


Fig. 1. (a) Temporal evolution of absorption and PL spectra of ZnSe QDs. Inset is the photograph of ZnSe QDs under UV light. (b) Absorption and PL spectra of ZnSe QDs prepared via microwave irradiation for 30 min (solid line) and oil-bath heating for 70 min (dashed line).

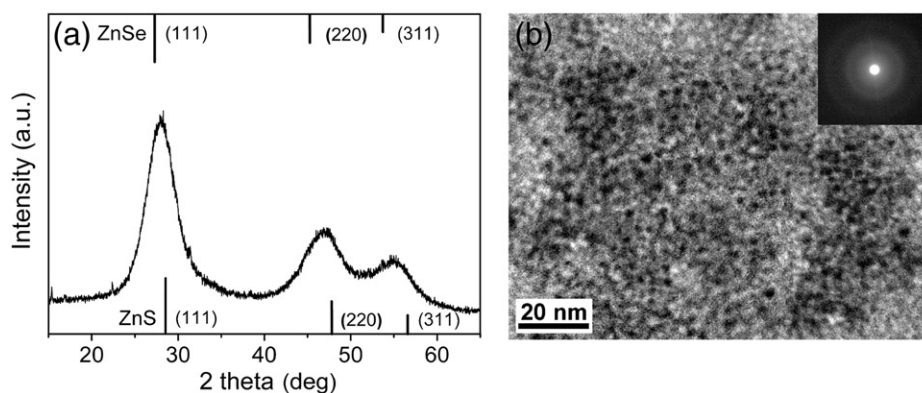


Fig. 2. (a) XRD pattern of ZnSe QDs. The vertical lines stand for the diffraction peaks of cubic ZnSe and ZnS. (b) TEM image and SAED pattern (inset) of as-prepared ZnSe QDs.

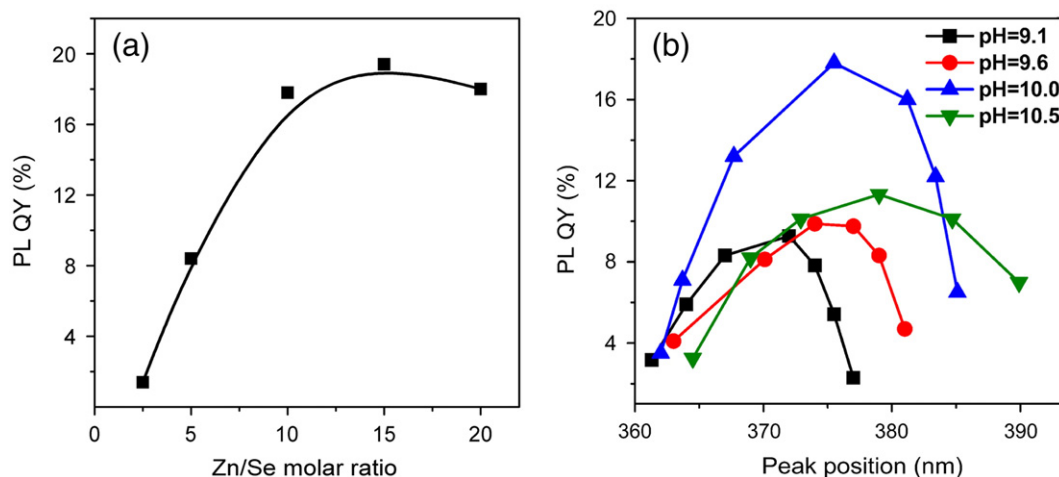


Fig. 4. PLQY of ZnSe QDs via (a) different Zn/Se molar ratios (pH = 10.0) and (b) PL peak positions under various pH values.

GSH/Zn molar ratios, intense trap emissions were also observed. We supposed that the relatively low concentration of 1:1 thiol–metal complex at high stabilizer concentrations would be responsible for the degraded surface quality of the QDs [15]. The corresponding PLQY of the ZnSe samples with different GSH/Zn molar ratios (Fig. 3 inset) further clarified the above speculations. Thus, a moderate GSH/Zn molar ratio at 1.8:1 was adopted for following experiments.

The effect of Zn/Se molar ratio on the PLQY of ZnSe QDs is illustrated in Fig. 4a. With the decreasing of Se molar fraction, the PLQY increased remarkably. Noticeably, when this ratio was below 5:1, red turbid would appear with prolonged heating, accompanied with low PLQY of the products. Yet when the ratio exceeded 10:1, further decrease of Se monomer amount showed minor improvement on the ZnSe luminescence. The explanation might be analogous to that of CdTe QDs [13]. The surface traps of ZnSe QDs which originated from Se dangling bonds would be occupied gradually by Zn–GSH complex with the increasing Zn/Se molar ratio, and a complete passivation to the QD surface would improve the PL performance best. Considering the output of ZnSe QDs, the Zn/Se molar ratio at 10:1 was appropriate for further work.

The pH dependent luminescence of ZnSe QDs was also studied in this work. As indicated in Fig. 4b, the resulting PLQYs under different pH values (from 9.1 to 10.5) all reached a maximum and then declined with the red-shift of QD emission wavelength. In this system, the pH at 10.0 favored higher PLQYs of the ZnSe QDs. The hydroxyl ions would enhance ZnSe luminescence by passivating the nonradiative centers on the QD surface [6], while an accelerated crystal growth at high pH value (10.5) would lead to more defects and surface states of the QDs [15], reflected by the depressed PLQY.

#### 4. Conclusions

In summary, we reported a one-step strategy for the aqueous synthesis of ZnSe QDs by microwave irradiation. The as-prepared QDs

possessed strong band-edge emitting (PLQY up to 18%), narrow size distribution (FWHM was 26–30 nm) and weak trap emission without post-treatments, which were attributed to the unique properties of microwave irradiation as well as controlled pH value and Zn/Se/GSH molar ratio. Compared with previous methods, this strategy was convenient and time saving, regardless of the pretreatment and oxidation of Se source. Meanwhile, this aqueous approach was reproducible and inexpensive that can be extended to large scale fabrication of high luminescent and water-soluble ZnSe QDs.

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