Photo-assisted synthesis of highly fluorescent ZnSe(S) quantum dots in aqueous solution

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This paper describes the synthesis of highly water-soluble and fluorescent ZnSe(S)-alloyed quantum dots (QDs). We used zinc perchlorate hexahydrate, sodium hydrogen selenide as precursors and mercaptopropionic acid as stabilizer to synthesize ZnSe QDs in aqueous solution at 160 °C for 9 h. The as-prepared ZnSe QDs possess a quantum yield (QY) of 8.1% and high trapped emission. After UV irradiation using a 100 W Hg–Xe lamp for 0.5 h, ZnSe(S) QDs having a QY of 19.0% are formed from ZnSe QDs. However, aggregation of ZnSe(S) QDs under longer UV irradiation (> 0.5 h) takes place, leading to instability and irreproducibility. To overcome this, additional thiol compounds (mercaptopropionic acid, mercaptosuccinic acid, 11-mercaptoundecanoic acid, and thioglycolic acid) were separately added to ZnSe QD solutions during UV irradiation. UV irradiation and oxygen accelerate the release of S^{2-} from the thiol compounds, leading to the formation of ZnSe(S) QDs. Among the thiol compounds, mercaptosuccinic acid is the most suitable in terms of stability and photoluminescence intensity. We suggest that the size and functional group of the thiol compounds play an important role in determining the optical properties and stability of ZnSe(S) QDs. The as-prepared ZnSe(S) QDs fluoresce strongly (QY up to 44.0%) at 407 nm with a narrow bandwidth ($W_{1/2} < 25$ nm) when excited at 325 nm.

Introduction

Semiconductor nanocrystals, also called quantum dots (QDs), have gained considerable interests because of their great potential in a wide range of applications such as sensing and cell imaging.[1–5] Having great photostability, high photoluminescence (PL) efficiency, size-dependent emission wavelengths when excited at the same wavelength, and sharp emission profiles, QDs have advantages over conventionally organic and inorganic fluorophores for labelling analytes of interest.[6,7] Water-soluble conjugated QDs that are easy for bio-modification have become one of the most important sensing materials for a great number of interesting biological analytes, including proteins,[8,9] DNA[10,11] and metal ions.[12]

There are fewer QDs that fluoresce below 450 nm than those that fluoresce over 450 nm. Among them, CdS, CdSe and ZnSe QDs are the most common.[13–17] CdS and CdSe QDs having the size-dependent absorption edge covering the entire visible region have been prepared in organic and aqueous solutions.[15–20] However, CdS and CdSe QDs exhibiting PL below 450 nm possess low quantum yields (QYs). In addition, the emission bands are usually broad, mainly because of a difficulty in controlling the size distribution when their sizes are small.[21] When compared to CdS and CdSe QDs, ZnSe QDs have advantages in blue UV region, including high PL QYs and stability. ZnSe nanomaterials having greater band gaps ranging from 2.8–3.4 eV (bulk ZnSe having a band gap of 2.7 eV) are interesting emitting materials over a region from UV to blue and have long been a choice of materials for fabrication of blue diode lasers.[22,23] Having such high and wide band gaps, ZnSe are also ideal for inorganic passivation of a variety of QDs to form core–shell QDs, such as CdSe–ZnSe and InAs–ZnSe QDs.[24,25] The core–shell QDs usually have higher QYs and greater stability than those of the original QDs (without shell) as a result of elimination of both anionic and cationic surface dangling bonds.

Bis(diethyldiselenocarbamato)zinc(II) and organometallic diethylzinc dissolved in tri-n-octylphosphine solutions were used to prepare $EtZnSe_2CNEt_2$, which was further subjected to thermolysis at 250 °C to form ZnSe QDs.[26] However, the precursors used are toxic and expensive. Alternatively, ZnO and selenium powder were used as zinc and Se precursors to prepare ZnSe QDs at 300 °C.[14] The thus-prepared ZnSe QDs emit light at 400–440 nm, with QYs in the range 6–10%. Because organic solutions were used in both cases, the thus-prepared ZnSe QDs show low aqueous solubility and are disadvantageous for biological applications. In order to overcome this limitation, ZnSe QDs are usually subjected to ligand exchange in solutions containing thiol-alkyl acids such as mercaptopropionic acid (MPA) and mercaptodecanoic acid.[27] These thiol-protected ZnSe QDs are water soluble and can be subjected to further bioconjugation. However, PL quenching often occurs after ligand exchange and/or bioconjugation.

So far, preparation of ZnSe QDs having high optical quality has not yet been achieved,[14,28,29] because of a difficulty in

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preventing the existence of a weak broad whitish-blue emission that is associated with their trap states. For example, ZnSe QDs prepared from Na_2SeSO_3 and $Zn(ClO_4)_2$ in aqueous solution exhibit a broad trap-emission band (350–600 nm), which leads to weak PL and poor optical resolution.[30,31] In order to overcome this, we prepared ZnSe QDs from selenium powder (99%) and $Zn(ClO_4)_2$ in aqueous solutions containing MPA, and then the thus-prepared ZnSe QDs were subjected to UV light irradiation (100 W Hg–Xe lamp). Irradiation of thiol-capped ZnSe QDs in aerated aqueous solution leads to the formation of ZnSe(S) QDs that have greater PL QYs and sharper emission band profiles. To understand the nature of the UV irradiation processes, the as-prepared ZnSe(S) QDs were characterized by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS).

Experimental

Chemicals

Selenium powder (99%), zinc perchlorate hexahydrate, MPA, thioglycolic acid (TGA) sodium salt, mercaptosuccinic acid (MSA, 97%), 11-mercaptoundecanoic acid (MUA, 95%), sodium borohydride (99%), and sodium hydroxide were obtained from Aldrich (Milwaukee, WI, USA). The water used in this study was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Preparation of sodium hydrogen selenide

Briefly, sodium borohydride (80.0 mg) was dissolved in 1 mL ultrapure water in a 20 mL glass vial, and then selenium powder (79.9 mg) was added. The 20 mL vial was sealed quickly with parafilm having a small hole allowing air circulation between the flask and atmosphere, and then was placed in an ice bath. A rapid reaction evolved hydrogen gas in the flask. Approximately 30 min later, the black selenium powder disappeared completely and NaHSe was formed.[32] The resulting clear aqueous solution was then transferred carefully, using a syringe, into 100 mL of degassed water in a volumetric flask sealed with a rubber plug. We wish to point out that NaHSe solution must be freshly prepared prior to use.

Preparation of MPA-stabilized ZnSe QDs

ZnSe QDs were synthesized through the addition of freshly prepared NaHSe solution to 1.0 mM N_2-saturated $Zn(ClO_4)_2$ solution (pH 10.5) in the presence of MPA as a stabilizer. The molar ratio of Zn^{2+} : HSe^- : MPA in the solution was 1 : 0.5 : 2.4. The mixture was then gently stirred and refluxed in a silicon-oil bath at 160 °C for 9 h.

UV irradiation of MPA-stabilized ZnSe QDs

To achieve high QYs, 10.0 mL of the as-prepared ZnSe QDs were mixed with aqueous solutions each containing one of the thiol compounds (MSA, MPA, TGA, or MUA). The final concentrations of the thiol compounds ranged from 0 to 25.0 mM. The mixtures were then subjected to illumination using a 100 W Hg–Xe lamp (model L 2442, Hamamatsu Photonics K. K., Shizuoka-Ken, Japan) at ambient temperature (25 °C) while being gently stirred. During irradiation, the vials were sealed with parafilm to avoid any loss of the solutions.

Characterization of ZnSe and ZnSe(S) QDs

The PL spectra of the as-prepared ZnSe and ZnSe(S) QDs were recorded using a fluorometer (F4500, Hitachi, Tokyo, Japan). The QYs of the ZnSe and ZnSe(S) QDs were determined by comparison with that (53%) of quinoline. Before TEM, HR-TEM, EDS, XPS and XRD measurements were conducted, the ZnSe and ZnSe(S) QDs were precipitated by adding 0.5 mL ethanol (100%) to the ZnSe and ZnSe(S) QD solutions (0.5 mL). The solutions were then subjected to centrifugation (16 500 rpm) for 20 min. to remove most excess thiol stabilizers. The precipitates were then suspended in 5.0 mM phosphate buffer (pH = 9.0). The sizes of the as-prepared ZnSe and ZnSe(S) QDs were measured using a JSM-1200EX II TEM system (JEOL Ltd., Tokyo, Japan). Prior to TEM measurements, ZnSe and ZnSe(S) QD solutions were gradually dropped onto 400-mesh carbon-coated copper grids and the excess solvent immediately evaporated. To confirm the contents of the elements of the as-prepared ZnSe and ZnSe(S) QDs, we conducted EDS measurements by using a LINK ISIS 300 spectrometer (Oxford Corp., UK) that was operated at 80 kV. XRD patterns were recorded using an X'Pert PRO system (PANalytical, Spectris plc, UK) with Cu Kα radiation. Prior to the XRD measurements, ZnSe and ZnSe(S) QDs (powders) were placed finely on quartz-glass supports. XPS measurements were performed on a VG ESCA210 electron spectroscope (VG Scientific Ltd., West Sussex, UK). All binding energies for different elements were calibrated with respect to C 1 s line at 284.6 eV.

Results and discussion

Preparation of ZnSe QDs

The as-prepared ZnSe QDs from NaHSe and $Zn(ClO_4)_2$ with molar ratio of 1 : 2 in aqueous solution containing MPA at ambient temperature and pressure exhibit PL QY lower than 1.0% at 405 nm when the excitation wavelength was set at 325 nm. In addition, the as-prepared ZnSe QDs exhibit a broad trap-emission band (400–600 nm), leading to weak PL and poor optical resolution. In order to further improve the quality (high QY and narrow size-distribution), we altered the synthesis conditions. On the basis of our previous study,[33] we tested the effect of temperature and solution pH. Through a series of experiments (temperature in the range 25–200 °C, and pH values in the range 6.5–10.5), we suggested that the optimum conditions are the temperature at 160 °C and pH value of 10.5 with respect to PL efficiency. Under these experimental conditions, the QY of thus-prepared ZnSe QDs increased to 8.1%, but a broad trap-emission band still existed, mainly due to the defects on their surfaces.[28] The mean size of the thus-prepared ZnSe QDs is 3.5 ($\pm$0.4) nm when 1000 QDs were counted.
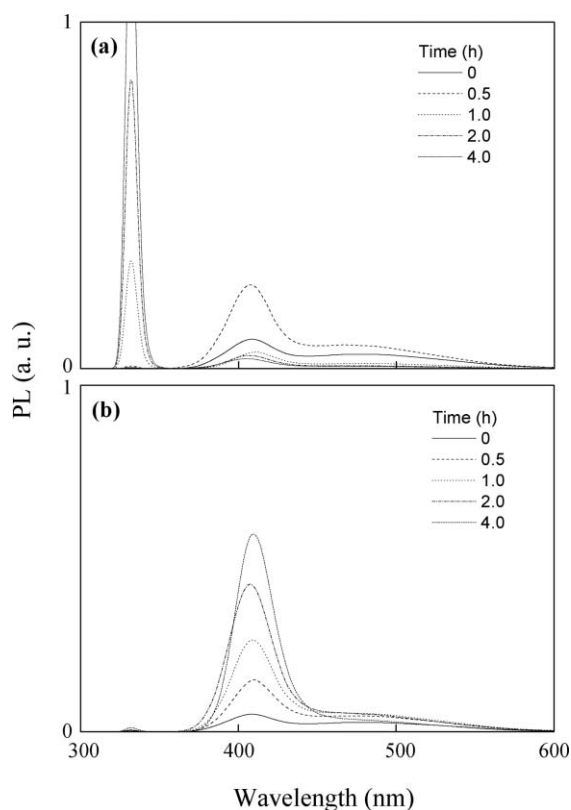
Fig. 1 Evolution of PL spectra of MPA-stabilized ZnSe QDs during UV irradiation. (a) 0 and (b) 7.5 mM MPA were additionally added to the ZnSe QD solution prior to irradiation using an Hg–Xe lamp (100 W). The excitation wavelength is 325 nm. The PL spectra are plotted as arbitrary units (a. u.).

UV Irradiation

In order to minimize the surface defects, the as-prepared ZnSe QDs were subjected to UV irradiation using an Hg–Xe lamp (100 W).[28,33–37] It has been reported that photo-etching and surface-recombination processes occur during UV irradiation, leading to enhancement of the PL properties of ZnSe QDs (enhancement of the band-edge emission and suppression of the trap emission).[28,34,38] Fig. 1(a) shows that the band-edge emission (QY 19.1%) and the trap emission both reach maxima after 0.5 h UV irradiation. With increasing irradiation

time (> 0.5 h), the QY of the as-prepared ZnSe QDs decreased mainly due to changes in surface properties as a result of photodecomposition of MPA. The strong scattering at 325 nm indicates the formation of QD aggregates, which was confirmed by the TEM measurement. The instability of the as-prepared ZnSe QDs (precipitates were formed after 1 h irradiation) also supported our reasoning. To prevent the formation of ZnSe QD aggregates, we added fresh 75.0 µL of MPA (7.5 mM) during irradiation. As exhibited in Fig. 1(b), the PL intensity increased with increasing irradiation time and reached a plateau (QY 47.2%) at 4 h. However, the trap emission (450–600 nm) also increased. We point out that the QY was almost constant if longer irradiation times (up to 12 h) were performed. MPA molecules stabilized the as-prepared ZnSe QDs through the binding of its oxygen atom and sulfur atoms to Zn sites (polygonal loops were formed).[39] Because of the existence of MPA, the as-prepared ZnSe QDs were more stable, as indicated by small scattering intensity around 325 nm.

Next, we investigated the effect of adding different thiol-stabilizers, including MPA, TGA, MSA, and MUA, during irradiation on the optical properties of ZnSe QDs. The ZnSe QD solutions containing MSA, MPA, TGA or MUA remained clear without precipitation after being subjected to UV irradiation for 4 h. Table 1 lists the optical properties of the as-prepared QDs after 4 h irradiation in the presence of additional stabilizers. The QDs that were prepared in the presence of additional MPA fluoresce stronger (about 4.6 fold) than those prepared after 0.5 h irradiation without adding additional MPA. However, the trap emission (450–600 nm) could not be suppressed effectively. When MUA was used instead of MPA as an additional stabilizer, the PL intensity of the as-prepared QDs is lower and the emission band is broader, mainly due to poor secondary coordination and water solubility. Interestingly, the trap-emission intensity can be totally suppressed when using TGA as an additional stabilizer. TGA has a carboxylic acid terminus as MPA has, but it is shorter by one methylene unit in structure. Thus, in addition to formation of the stable hexagonal configuration (one TGA can coordinate with two Zn sites), the carbonyl group of TGA allows absorption of free Zn^{2+} ions from the surroundings and places them on the Se sites.[39] As a result, the surface defects reduced. However, the secondary coordination

Table 1 Impact of thiols (7.5 mM) on the color and PL property of ZnSe(S) QDs after 4 h irradiation using a 100 W Hg–Xe lamp

Additional stabilizer	None	MPA	TGA	MSA	MUA
Structure	—				
Color	Limpid red	Clear	Clear	Clear	Clear
λ_{em}/nm	405	410	411	409	411
$I_{band\ edge}/I_{trap\ emission}{}^{a}$	4.1	15.4	16.1	19.0	0.7
PL enhancement[b]	1.0	4.6	1.8	2.9	0.5

[a] The ratio between the intensity of band edge emission (λ_{em}) and trap emission (470 nm). [b] The intensity of band-edge emission for different stabilizers compared to that without additional stabilizer (irradiation time 0.5 h).
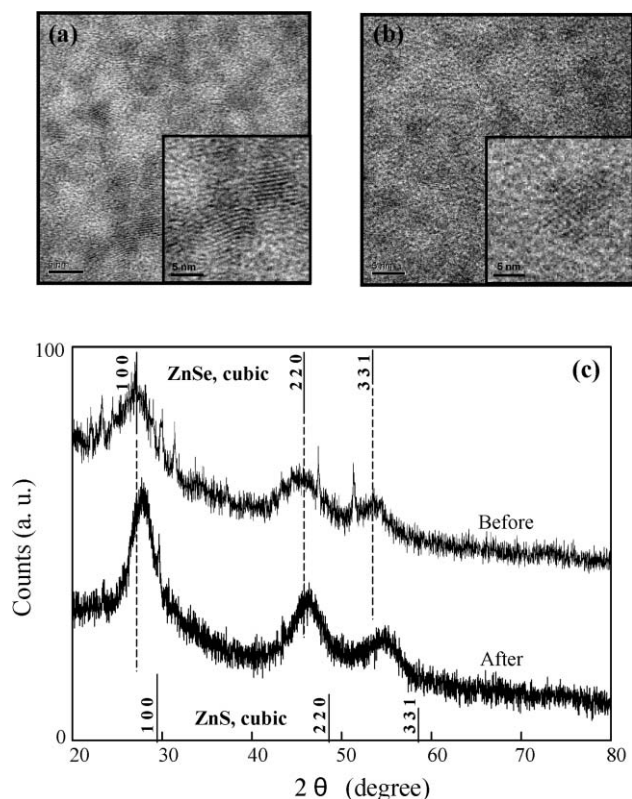
Fig. 2 HR-TEM images and XRD patterns of MSA-stabilized ZnSe QDs and ZnSe(S) QDs. TEM images: (a) ZnSe QDs and (b) ZnSe(S) QDs. XRD patterns: (c) the concentration of MSA is 10.0 mM. Irradiation time is 4 h. Other conditions are the same as in Fig. 1.

of TGA is not beneficial for preparation of QDs having greater QYs. The molecular structure of MSA combines both the features of MPA and TGA. As expected, the PL intensity enhanced about 2.9 fold and the trap emission reduced when MSA was used as an additional stabilizer.

In order to further investigate the role of MSA on improving the optical properties, the QDs before and after UV irradiation were subjected to different spectrochemical analyses. The TEM images depicted in Fig. 2(a) and 2(b) show that the sizes of QDs before and after UV irradiation are 3.5 ($\pm$0.4) nm and 3.6 ($\pm$0.4) nm, respectively. The results confirm that no red shifts in the band edge of the UV-absorption and PL spectra were observed after UV irradiation.[28] However, the XRD patterns displayed in Fig. 2(c) exhibit a shift from their original position for ZnSe to ZnS structure after UV irradiation, which indicated that sulfur entered the crude ZnSe structure gradually and then ZnSe(S) alloy structure was formed.[28,29]

Further evidence of the incorporation of sulfur into ZnSe structure is demonstrated by the EDS spectra depicted in Fig. 3(a) and 3(b). The S/Zn and Se/Zn ratios of the QDs before and after UV irradiation increased from 3.1 to 3.5 and decreased from 0.7 to 0.5, respectively (the Zn components were kept constant). From the results, we estimated the x value of ZnS_xSe_{1-x} is 0.8. The XPS spectra depicted in Fig. 3(c) and 3(d) show that the intensity of Se $3d_{5/2}$ binding energy (54.4 eV) decreased and the intensity of S 2p binding energy (163.5 eV) increased after 4 h irradiation of the as-prepared ZnSe

QDs.[40,41] The XPS results support that the amount of Se decreased, while that of S increased after UV irradiation. Based on this result, we conclude that alloyed ZnSe(S) QDs were prepared.

Possible mechanism

The formation of alloyed ZnSe(S) from ZnSe QDs were believed to be the result of several reactions.[29] In the air, the outmost layer of ZnSe QDs under UV irradiation is decomposed to form Zn^{2+} ion and SeO_2, as shown in eqn (1). As expressed in eqn (2), sulfide ions were produced from MSA in alkaline solution after UV irradiation.

$$ZnSe + O_2 \xrightarrow{hv} Zn^{2+} + SeO_2 \qquad (1)$$
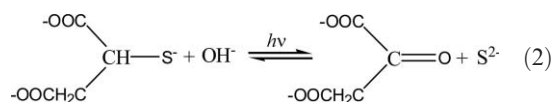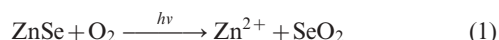
Then, the produced Zn^{2+} and S^{2-} combined to form ZnS on the ZnSe QDs, that then underwent reconstruction to form ZnSe(S) QDs. It is noted that the binding strength of Zn^{2+} toward S^{2-} is greater than that toward Se^{2-}.

In order to further support our proposed mechanism, we investigated the effect of MSA concentration on the preparation of ZnSe(S) QDs. With increasing additional MSA concentration from 0 to 10.0 mM, the QYs of as-prepared ZnSe(S) QDs increased from 2.8% (without additional MSA, ZnSe(S) QDs aggregated after UV irradiation for 4 h) to 44.0% and the full width at half maximum ($W_{1/2}$) decreased from 42 nm to 25 nm as listed in Table 2. At low concentrations (< 5.0 mM), the thus-prepared ZnSe(S) QDs possess low QYs and greater trapped emission. This is mainly due to the formation of QD aggregates and lower content of S in the ZnSe(S) QDs. At high concentrations (25.0 mM), the QY of the thus-prepared ZnSe(S) QDs is low, mainly because greater amounts of NaOH were added to adjust pH value. The narrower emission peak profile is due to surface reconstruction that leads to a narrower size-distribution of the as-prepared ZnSe(S) QDs. We point out that the emission wavelengths (around 405 nm) of the thus-prepared ZnSe(S) QDs only slightly changed at different MSA concentration. We also investigated the effect of irradiation power on the optical properties of ZnSe(S) QDs. Under photo-irradiation for 1 h, an Hg–Xe lamp with an output of 500 W allowed the preparation of ZnSe(S) QDs, having greater PL intensity (QY 36.0%) than that with an output of 100 W (9.0%). However, further increasing irradiation using an Hg–Xe lamp with an output of 500 W did not produce ZnSe(S) QDs with higher QYs. The result further supports our proposed mechanism; photo-etching and recombination processes take place under UV irradiation

Conclusions

In this paper, we describe a simple route to prepare ZnSe(S) QDs that fluoresce strongly in blue-UV region (λ_{em} = 405 nm). Under UV irradiation, ZnSe(S) QDs were formed from ZnSe QDs in the presence of thiol compounds. The release of S^{2-}
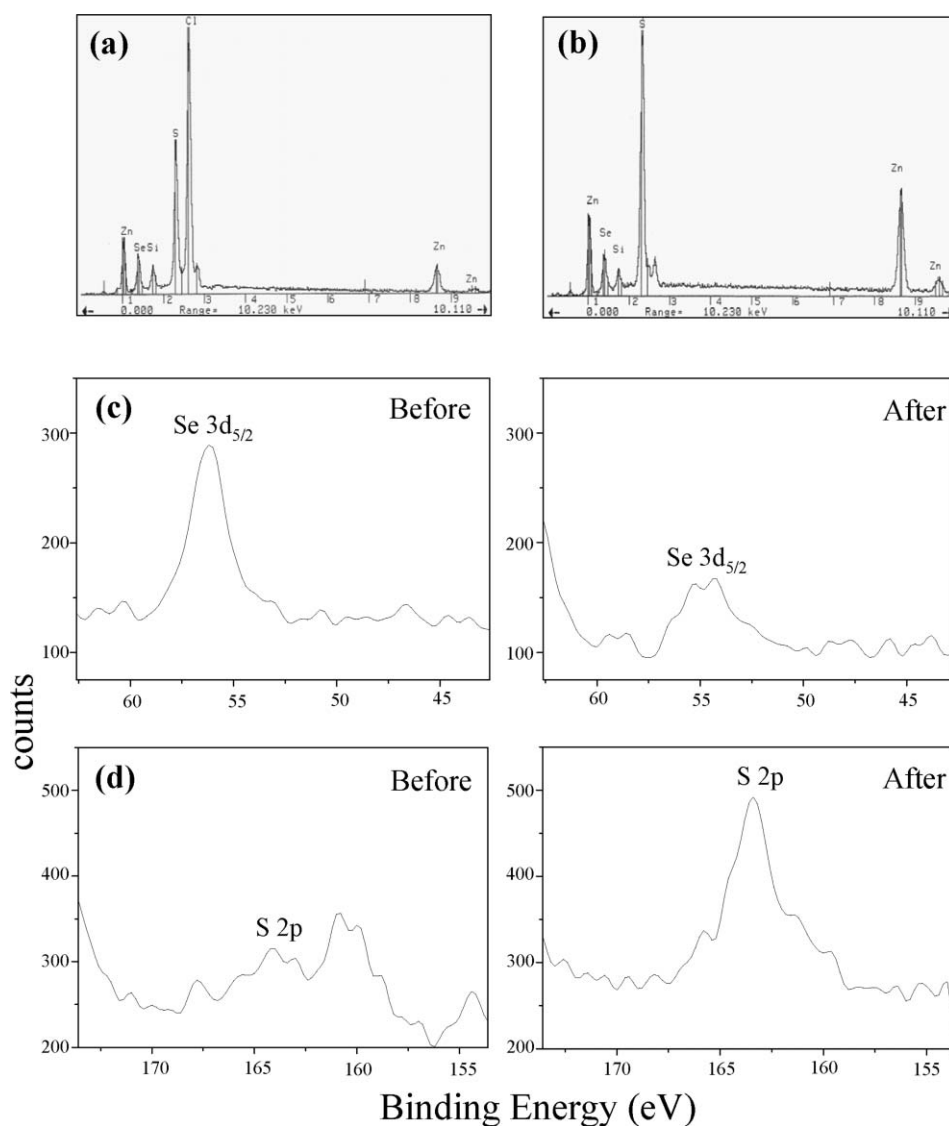
Fig. 3 EDS and XPS spectra of MSA-stabilized ZnSe QDs and ZnSe(S) QDs. EDS spectra: (a) ZnSe QDs and (b) ZnSe(S) QDs. XPS spectra: (c). Se 3d$_{5/2}$ binding energy (54.4 eV) and (d) S 2p binding energy (162.3 eV) before and after irradiation for 4 h. Other conditions are the same as in Fig. 1.

Table 2 Impact of MSA concentration on the PL property of ZnSe(S) QDs after 4 h irradiation using a 100 W Hg–Xe lamp

	ZnSe(S) QDs		
Concentration of MSA (mM)	λ_{em}/nm	$W_{1/2}$/nm	QY (%)
0	406	42	2.8
2.5	407	28	8.5
5.0	408	27	9.4
7.5	409	26	36.0
10.0	407	25	44.0
25.0	405	32	18.1

from the capping agents (thiol compounds) was accelerated by UV irradiation and oxygen. We have demonstrated that the size and functional group of the thiol compounds play an important role in determining the stability and optical properties of ZnSe(S) QDs. Among the tested thiol compounds, MSA is superior in terms of high PL QY and low trapping emission. The thus-prepared ZnSe(S) QDs are stable, highly fluorescent, and less toxic than CdSe QDs. With such a high QY and narrow emission profile, we expect that the thus-prepared ZnSe(S) QDs should become useful sensing and lasing materials.

Acknowledgements

References

1 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
2 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 41.
3 H. Weller, *Adv. Mater.*, 1993, **5**, 88.
4 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, 1995, **7**, 607.
5 A. P. Alivisatos, *Science*, 1996, **271**, 933.

6 Y. Chan, J. P. Zimmer, M. Stroh, J. S. Steckel, R. K. Jain and M. G. Bawendi, *Adv. Mater.*, 2004, **16**, 2092.

7 C. Li and N. Murase, *Langmuir*, 2004, **20**, 1.

8 L. Shi, N. Rosenzweig and Z. Rosenzweig, *Anal. Chem.*, 2007, **79**, 208.

9 Y. Chen, T. Ji and Z. Rosenzweig, *Nano Lett.*, 2003, **3**, 581.

10 R. Robelek, F. D. Stefani and W. Knoll, *Phys. Status Solidi A*, 2006, **203**, 3468.

11 S. Pathak, S.-K. Choi, N. Arnheim and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4103.

12 Y. Chen and Z. Rosenzweig, *Anal. Chem.*, 2002, **74**, 5132.

13 X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science*, 2005, **307**, 538.

14 H.-S. Chen, B. Lo, J.-Y. Hwang, G.-Y. Chang, C.-M. Chen, S.-J. Tasi and S.-J. J. Wang, *J. Phys. Chem. B*, 2004, **108**, 17119.

15 Y. C. Cao and J. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 14336.

16 B. A. Harruff and C. E. Bunker, *Langmuir*, 2003, **19**, 893.

17 Z. Deng, L. Cao, F. Tang and B. Zou, *J. Phys. Chem. B*, 2005, **109**, 16671.

18 A. E. Raevskaya, A. L. Stroyuk and S. Y. Kuchmiy, *J. Colloid Interface Sci.*, 2006, **302**, 133.

19 L. Qu and X. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 2049.

20 J. Jasieniak, C. Bullen, J. van Embden and P. Mulvaney, *J. Phys. Chem. B*, 2005, **109**, 20665.

21 D. V. Talapin, A. L. Rogach, E. V. Shevchenko, A. Kornowski, M. Haase and H. Weller, *J. Am. Chem. Soc.*, 2002, **124**, 5782.

22 M. A. Hines and P. Guyot-Sionnest, *J. Phys. Chem. B*, 1998, **102**, 3655.

23 S. B. Mirov, V. V. Fedorov, K. Graham, I. S. Moskalev, V. V. Badikov and V. Panyutin, *Opt. Lett.*, 2002, **27**, 909.

24 N. Myung, Y. Bae and A. J. Bard, *Nano Lett.*, 2003, **3**, 1053.

25 Y. Cao and U. Banin, *J. Am. Chem. Soc.*, 2000, **122**, 9692.

26 N. Revaprasadu, M. A. Malik, P. O'Brien, M. M. Zulu and G. Wakefield, *J. Mater. Chem.*, 1998, **8**, 1885.

27 N. Pradhan, D. M. Battaglia, Y. Liu and X. Peng, *Nano Lett.*, 2007, **7**, 312.

28 A. Shavel, N. Gaponik and A. Eychmüller, *J. Phys. Chem. B*, 2004, **108**, 5905.

29 H. Qian, X. Qiu, L. Li and J. Ren, *J. Phys. Chem. B*, 2006, **110**, 9034.

30 V. V. Nikesh and S. Mahamuni, *Semicond. Sci. Technol.*, 2001, **16**, 687.

31 N. Murase, M. Y. Gao, N. Gaponik, T. Yazawa and J. Feldmann, *Int. J. Mod. Phys. B*, 2001, **15**, 3881.

32 D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 197.

33 Y.-W. Lin, M.-M. Hsieh, C.-P. Liu and H.-T. Chang, *Langmuir*, 2005, **21**, 728.

34 N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 7177.

35 M. Jones, J. Nedeljkovic, R. J. Ellingson, A. J. Nozik and G. Rumbles, *J. Phys. Chem. B*, 2003, **107**, 11346.

36 H. Bao, Y. Gong, Z. Li and M. Gao, *Chem. Mater.*, 2004, **16**, 3853.

37 N. P. Osipovich, A. Shavel, S. K. Poznyak, N. Gaponik and A. Eychmüller, *J. Phys. Chem. B*, 2006, **110**, 19233.

38 D. V. Talapin, N. Gaponik, H. Borchert, A. L. Rogach, M. Haase and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 12659.

39 H. Zhang, D. Wang and H. Möhwald, *Angew. Chem., Int. Ed.*, 2006, **45**, 748.

40 W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie and Y. Qian, *J. Am. Chem. Soc.*, 1999, **121**, 4062.

41 G.-T. Zhou, X. Wang and J. C. Yu, *Cryst. Growth Des.*, 2005, **5**, 1761.