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[Chemistry and Chemical Engineering]

## Impact of surface passivation and modification on II-VI QDs recovered from reverse micelle template<sup>†</sup>

QIU Qi<sup>1,2</sup>, LI Yin-jian<sup>1</sup>, LU Wei-zhong<sup>1</sup>, and LUO Zhong-kuan<sup>1</sup>

1) College of Chemistry and Chemical Engineering 2) State Key Laboratory of Silicon Materials  
Shenzhen University Zhejiang University  
Shenzhen 518060 Hangzhou 310027  
P. R. China P. R. China

**Abstract:** The successful extractions of ZnMnSe as well as ZnSe quantum dots (QDs) from a reverse micelle template were reported. The recovered QDs kept their functionality with distinct enhancement in photoluminescence. After being coated with a possible layer of Zn(OH)<sub>2</sub> within the template, the QDs were extracted from the template by adding water to induce phase transition and employing specific organic solvent. Thereafter, the extracted QDs were capped with mercapto-undecanoic acid for dispersion in water to render crystal clear solution. Analytical techniques such as X-ray diffraction, transmission electron microscopy, dynamic light scattering, and fluorometer were employed to characterize the crystal structure, morphology, average particle size, and photoluminescence of the samples. The mechanism of the surface protection towards QDs was investigated and discussed. A mechanism was proposed as block copolymer molecular being adsorbed to the QDs surface that retards the oxidation process of QDs during the extraction. Consequently, the extracted QDs demonstrated invariable photoluminescence and consistent stability for months.

**Key words:** isolation and purification; quantum dots; photoluminescence; reverse micelle template; block copolymers; transition metal doping; surface modification; surface passivation

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QDs with doped ions of transition metals have attracted significant attention for their potential in tuning the emission wavelength to a longer one than the corresponding bulk gap emission<sup>[1-3]</sup>. Doped QDs could be useful as multi-color tags for biological imaging<sup>[4]</sup> and sensing application<sup>[5]</sup>. Moreover, magneto-optical QDs could be developed for spintronic applications. There have been tremendous reports<sup>[6-8]</sup> on the synthesis. Nevertheless, further application of the materials requires successful recovery of QDs from the templates and appropriate protection through surface modification to avoid oxidation, especially from reverse micelle template.

A reverse micelle-based synthesis technique were previously

reported<sup>[9]</sup> to dope transition metal ions into II-VI QDs at the room temperature. The surfactant is a triblock copolymer, quite different from regular surfactant. This surfactant can form rich polymorphism under room temperature. This easily scale-up process employs less expensive chemicals compared with hot injection technique. The stabilization mechanism on recovery and surface treatment process were investigated according to the results from equipment analyses. A procedure was developed to extract QDs from reverse micelle template. The ability to transform QDs from hydrophobic to hydrophilic is essential for any bio-applications. Ultimately, the removed QDs were capped with functional hydrophilic ligands and stabilized in aqueous solution.

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作者简介: 邱琦(1976-), 女(汉族), 江苏省宜兴市人, 深圳大学讲师、博士. E-mail: chwchi@gmail.com

通讯作者: 罗仲宽(1962-), 男(汉族), 深圳大学教授. E-mail: luozhongkuan@126.com

## 1 Experiments

All chemicals were of analytical grade and used as received.

### 1.1 Recovery of QDs

Following our reported synthesis<sup>[9]</sup>, the QDs were extracted from the template and rendered water dispersible. The procedure depicted below is applicable to QDs from reverse micelle as well as liquid crystal template.

The reverse micelle was fully mixed with certain volume of nanopure water to render phase separation. Subsequently, the mixture was centrifuged and separated into three distinct phases. Under illumination of UV-lamp as well as photoluminescence (PL) scans, only the thin middle white gel-like layer contained QDs. The type and ratio of solvent is essential for successful recovery of QDs from the template. Two solvents, named solvent A and solvent B, were compared in this study. The extraction results revealed that solvent A performed better than solvent B. The solvent A was employed for extraction of QDs from 2 mL of reverse micelle. The dispersion was centrifuged to acquire the deposit of QDs. Eventually, the supernatant was decanted and deposit was transferred to a glass vial for subsequent surface modification.

### 1.2 Surface passivation and modification of QDs

An aliquot of the sample was taken out for surface coating. The details are as follows: 1.5 mol/L  $\text{Zn}(\text{AcO})_2$  solution was added to the microemulsion. The amount of  $\text{Zn}(\text{AcO})_2$  ranged from 16% to 100% as compared to the precursor zinc acetate in the template. Subsequently, the mixture was magnetic stirred overnight. As expected, a layer of zinc hydroxide was formed around each QDs. Through the surface passivation procedure, a layer of possibly  $\text{Zn}(\text{OH})_2$  was coated around the QDs before extraction from the reverse micelle template.

The main purpose of the surface passivation is to amend the defects on surface of QDs and retard the oxidation of QDs in the air. The extracted compound semiconductor QDs is hydrophobic in nature. Consequently, the surface modification is essential to render water dispersibility for potential application as biotagging. A reported procedure<sup>[10]</sup> was modified. The recovered QDs were dispersed in nanopure water to obtain 2 mL of aqueous solution.

### 1.3 Characterizations

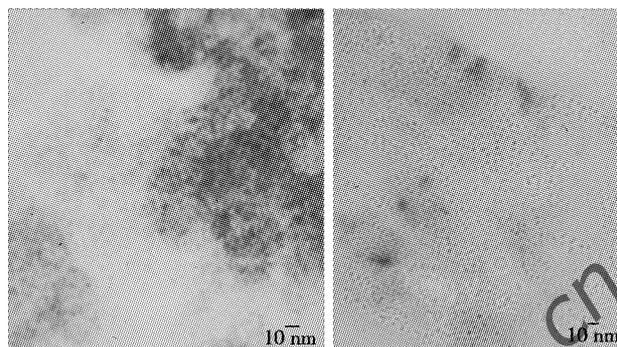
X-ray diffraction (XRD, X-pert B523-Banalytical,  $\lambda = 0.154$  nm, CuK irradiation) was performed to obtain the crystal structure of the QDs. The photoluminescence was recorded by a spectrofluorometer (Fluorolog 3, Jobin Yvon, Horiba) equipped with Xenon lamp. The measured sample, held in a 12 mm borosilicate culture tube was excited at 320 nm. The spectra were re-

corded in the range of 350 ~ 625 nm. Transmission electron microscopy (TEM, JEOL 3010) was employed to characterize the morphology of the QDs. Dynamic light scattering was performed to estimate the size of dispersed phase in water using a model Model 127 Stabilite Helium-Neon Laser (Spectra-Physics lasers Co.) with a ALV/SO-SIPD small outline single photon detector operating at an angle of 90°.

## 2 Results and Discussions

### 2.1 TEM images

TEM image in Fig 1 (a) shows average size of ZnSe QDs about 3 nm, consistent with 2.7 nm estimated from our reported formula<sup>[11]</sup>. The image of the nanoparticles was blurred due to the surrounding block copolymer. After extraction from the template, the QDs were well dispersed in water without agglomeration as seen in Fig 1 (b). The samples in both figures were prepared from  $\text{Zn}(\text{AcO})_2$  precursor of 0.1 mol/L.



(a) In microemulsion (b) In water, passivated

Fig. 1 TEM images of ZnSe QDs

图 1 ZnSe 量子点的 TEM 图

The extracted ZnSe: Mn QDs self assembled into nanowires as seen from Fig 2. Precursor concentration of  $\text{Zn}(\text{AcO})_2$  was 0.45 mol/L with  $x = 0.1$ . A plausible explanation is that the triblock copolymer macromolecular adsorbed to the QD surface and induced self assembly of the extracted QDs. This observation explains why QDs in this case could be stable over extended period of time even in the atmosphere. With the protection of triblock copolymer molecules, QDs could be recovered from the template with minimum oxidation.

Fig 3 (a) and Fig 3 (b) show the images of the water-dispersed ZnMnSe (precursor concentration of  $\text{Zn}(\text{AcO})_2$  was 0.45 mol/L with  $x = 0.1$ ) without and with surface passivation respectively. The average diameters of the dispersed phase in both figures are in the range of 24 ~ 28 nm. There was a circle layer around the QDs. This outer layer was speculated to contribute to unreacted  $\text{Mn}(\text{AcO})_2$  and leftover block copolymer. Since organic

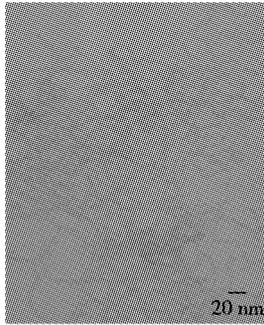


Fig. 2 TEM image of recovered ZnMnSe QDs before dispersed in water

图 2 提取 ZnMnSe 量子点分散于水前的 TEM 图

or macromolecular materials are nearly transparent under the high voltage electronic bombard, the block copolymer and MUA molecules appear invisible under TEM. The length of one MUA molecular was estimated by adding the lengths of all covalent bonds. Assuming linear morphology, we could obtain the molecular length of MUA as about 1.9 nm. Accordingly, the diameter of the dispersed phase in water should be about 28 ~ 32 nm. Further DLS measurements determined the average size of the dispersed phase in water as ~ 35 nm with a relatively narrow size distribution. This small discrepancy between estimated and measured size might be from the impact of solvent within the dispersed phase as well as the MUA molecules conjugated surrounding the water-dispersed QD surface. Moreover, MUA has its own spatial conformation leading to molecular length shorter than that of a linear one. For TEM analysis, samples were dried to get rid of water within the dispersed phase. This loss of water led to a decrease in size of the dispersed size<sup>[12]</sup> as shown in Fig 3.

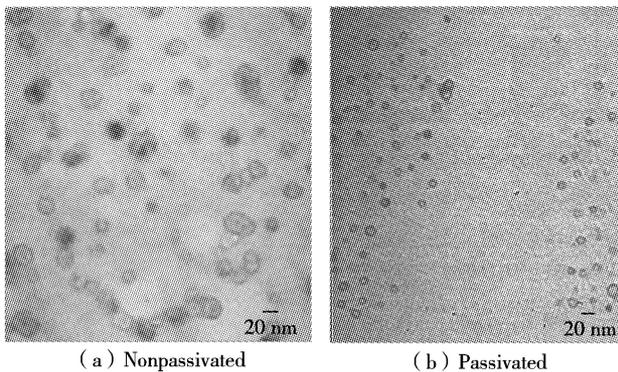


Fig. 3 TEM picture of ZnMnSe QDs dispersed in water

图 3 分散于水中的 ZnMnSe 量子点的 TEM 图

Fig 4 reveals an evident inorganic layer circling around the ZnMnSe QD with probable block copolymer interspaces. This inorganic layer was not observed for undoped ZnSe QDs as seen in Fig 1(b). We have previously reported<sup>[9]</sup> that the doped  $Mn^{2+}$

was not proportional to the  $Mn^{2+}$  concentration in the precursor solution. Besides, it was also confirmed that MnSe compound could not be formed under the synthesis condition in this investigation. It was therefore postulated that the free  $Mn^{2+}$  could be adsorbed on the surface of the polymer to form an inorganic/organic hybrid layer surrounding the QDs. The mechanism is still under further investigation.

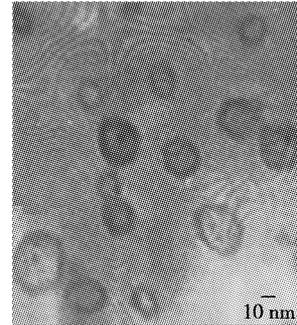


Fig. 4 TEM picture of QDs in Fig 3(b) at higher magnitude

图 4 QDs 图 3(b) 放大 TEM 图

## 2.2 Characterization by XRD patterns

The XRD diffraction patterns of extracted ZnSe and ZnMnSe QDs are plotted in Fig 5. The patterns present three fingerprint peaks at  $27^\circ$ ,  $46^\circ$ , and  $53^\circ$ , matching the standard peaks corresponding to diffraction angles from the [111], [220], and [311] planes of cubic (zinc blend) ZnSe. This observation reveals that the QDs extracted from the template keep the original crystalline phase. The QD size of ZnMnSe calculated by Debye-Scherrer formula, ~2.2 nm, from [220] plane in the diffraction pattern agrees well with the results by TEM pictures.

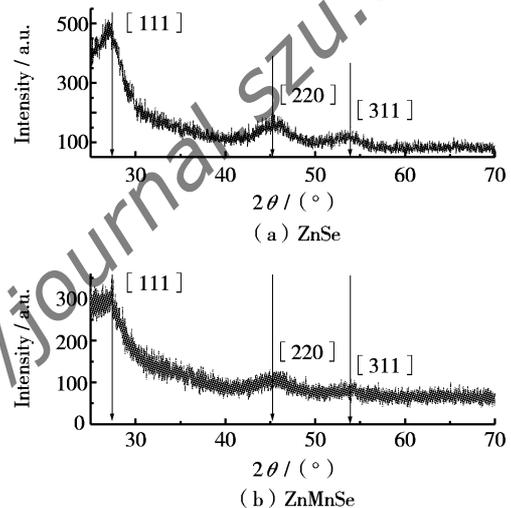


Fig. 5 X-ray diffraction patterns of QDs

图 5 量子点的 XRD 衍射图

### 2.3 PL spectra

To passivate the surface of QDs directly in the template is a feasible procedure to increase the stability of the QDs for better recovery. The passivated sample together with the control sample was measured for PL with spectra presented in Fig 6(a). Precursor concentration of  $\text{Zn}(\text{AcO})_2$  was 0.45 M with  $x = 0.1$ , aged for 7 days. Since the added  $\text{Zn}(\text{AcO})_2$  was concentrated and in very small volume as compared to the reaction volume, the microemulsion was still stable and no phase separation was observed. The coating process took overnight. Both samples in the figure are from the same batch of product. The spectrum with bar symbol is the coated sample. Fig 6(a) shows no obvious shift of the ZnSe PL peak under surface passivation from concentrated  $\text{Zn}(\text{AcO})_2$ . Furthermore, the coated ZnMnSe shows enhanced PL intensity over time, see Fig 6(b). This significant increase in the PL suggests the stabilization of the surface of the QDs. It is speculated that the added  $\text{Zn}(\text{AcO})_2$  became diluted within the water pool in the microemulsion and reacts on the surface of the existing QDs to form a layer of  $\text{Zn}(\text{OH})_2$  surrounding the NPs. This distinct enhancement in the band-edge PL intensity originates from the remarkable reduction of nonradiative recombination processes, which usually result in a very short decay time, due to surface defects of QDs<sup>[13]</sup>.

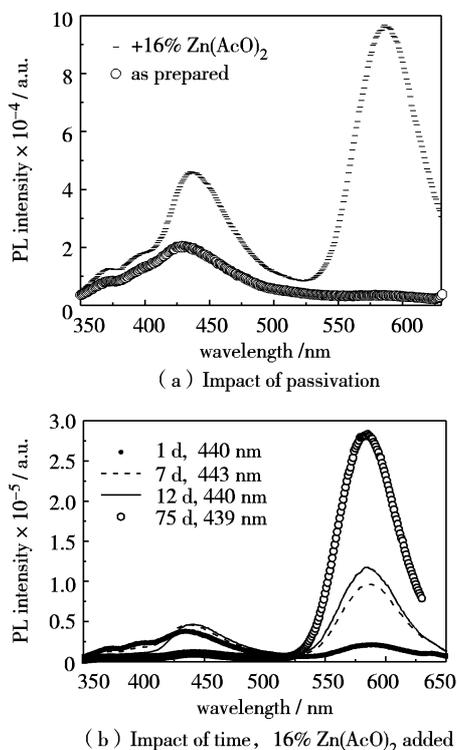


Fig. 6 PL spectra of ZnMnSe  
图 6 ZnMnSe 的荧光光谱

The QDs can be successfully recovered by phase separation of the reverse micelle. The composition change in the template enabled the mixture to move to two-phase area in phase diagram. Most of the p-xylene solvent and part of the Pluronic P105 surfactant can then be partially cleaned from the nanoparticle layer by washing carefully with solvent A. The spectra in Fig 7 compare the PL of the prepared QDs with that of the sample dispersed in water. There is a remarkable increase in the PL intensity after recovery of both ZnSe (Fig. 7(a)). The increase in PL of the extracted QDs could be probably due to the surface modification of the ligand conjugation. This surface modification could eliminate potential surface defects and therefore stabilize the QDs. Another reason for this increase in spectra intensity could be possibly contributed to the dilution effect on the photoluminescence of ZnSe quantum dots<sup>[9]</sup>. The optimal particle concentration yielding the maximum emission intensity increases as the particle size decreases. This observation should be applicable to recover other QDs in similar systems. For example, we also recovered doped ( $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$ ) quantum dots from the reverse micelle template. The QDs dispersed in water showed similar distinct increase in the photoluminescence intensity, see  $\text{Mn}^{2+}$  doped QDs in Fig 7(b).

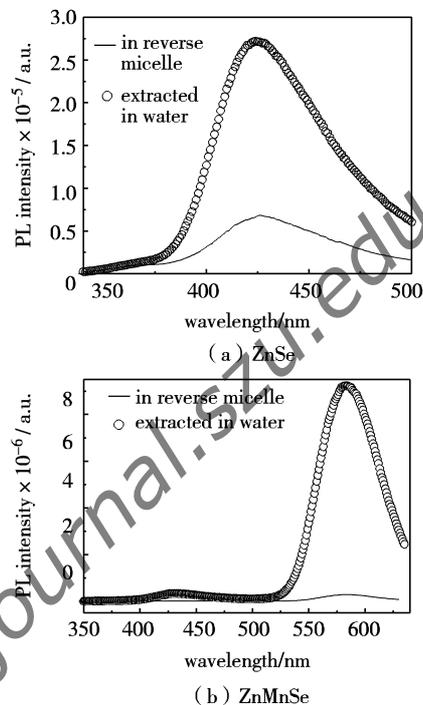


Fig. 7 PL spectra of extracted QDs dispersed in water compared with a prepared sample  
图 7 微乳液和水中分散的量子点的荧光光谱

Ultimately, preliminary investigation on electrophoresis was performed on ZnSe QDs conjugated with DNA molecules as well

as compared with that of free DNA and free ZnSe QDs dispersed in water (not shown). Free DNA swam the fastest in the electrophoresis. The conjugated DNA was slow in swimming with much stronger photoluminescence detected. Consequently, this above mentioned surface modification and recovery process is an effective way to obtain stable and water dispersible ZnSe QDs for practical application.

## Conclusions

ZnMnSe QDs were successfully recovered from a reverse micelle template consisting of p-xylene, water, and a triblock copolymer. Surface of the QDs was passivated with Zn(OH)<sub>2</sub> prior to extraction to amend potential surface defects and prevent possible oxidation. The passivated QDs showed distinct increase in PL with no evident shift. The QD extraction from the template was performed by adding water and inducing phase transition. TEM analysis suggested that recovered QDs were surrounded by a layer of block copolymer as well as undoped Mn<sup>2+</sup>. The extracted QDs were subsequently capped with mercapto-undecanoic acid or dihydrolipoic acid and dispersed in water to render crystal clear solution. Analytical techniques such as XRD, TEM, DLS, and fluorometer were employed for characterization. The extracted QDs demonstrated invariable emission spectra and consistent stability for months. This process is applicable to extract nanoparticles from other forms of template (such as liquid crystal template) and to keep their functionality. In conclusion, the technology has the potential for practical application of the QDs in numerous areas, such as biotagging, spintronics, and etc.

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【化学与化工】

## 表面处理对反相微乳液中 II-VI 族量子点的影响

邱琦<sup>1,2</sup>, 李迎建<sup>1</sup>, 吕维忠<sup>1</sup>, 罗仲宽<sup>1</sup>

(1. 深圳大学化学与化工学院, 深圳 518060; 2. 浙江大学硅材料国家重点实验室, 杭州 310027)

**摘要:** 以对二甲苯为连续相, 水为分散相, 聚(氧乙烯)-聚(氧丙烯)-聚(氧乙烯)嵌段聚合物为表面活性剂, 制备 ZnSe 和 ZnMnSe 量子点. 在量子点表面覆盖一层 Zn(OH)<sub>2</sub> 使其发生钝化, 再加水引起相分离, 选择合适的有机溶剂可从反相微乳液中成功分离出上述量子点, 分离后的量子点保持荧光特性且量子点荧光有显著增强. 经 11-巯基十一烷酸表面修饰, 分离的量子点可分散在水中形成透明溶液. 采用 X-射线衍射、透射电镜、动态激光光散射和荧光光度计表征晶体结构、形貌、尺寸分布和荧光特性, 讨论了使量子点稳定的表面保护机理. 研究表明, 嵌段聚合物分子吸附在量子点表面, 阻碍了其氧化进程, 表面钝化可修补晶体部分缺陷, 使分离的量子点荧光增强, 稳定期达数月之久.

**关键词:** 分离与提纯; 量子点; 光致发光; 反相微乳液; 嵌段聚合物; 过渡金属掺杂; 表面修饰; 表面钝化

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