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Biomimetic Synthesis of CdSe Quantum Dots through Emulsion Liquid Membrane System of Gas-Liquid Transport

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The cadmium selenide quantum dots (QD) have been synthesized by template-control in an emulsion liquid membrane system. The system consisted of kerosene as solvent, L152 (dialkylene succinimide) as surfactant, N7301 (trialiphatic amine, R_3N, $R=C_8—C_{10}$) as carrier, 0.1 mol/L $CdCl_2$ solution as internal-aqueous phase and H_2Se gas as external phase. Additive organic template agent in internal-aqueous phase was necessary to form CdSe QD. The influence of the nature of template and its concentration on sizes of the formed CdSe QD has also been studied. Transmission electron microscopy showed that the sizes of the products could be controlled down to 3—4 nm. X-ray diffraction analysis revealed that the crystals had cubic structure. The formation process and the optical properties of CdSe QD have also been presented.

Keywords emulsion liquid membrane, CdSe, quantum dot, template-control, nanoparticle, biomimetic synthesis

Introduction

Semiconductor nanocrystals or quantum dots (QD) with dimensions smaller than the exciton Bohr radius exhibit unique quantum size effect and strong size-dependent electronic, magnetic, optical properties.[1-4] Over the years, CdSe QD have been used for a wide range of applications in biological label,[5] cellular imaging,[6] electronic device,[7] lasers,[8] light emitting diodes and photovoltaic solar cells.[9] So, the synthesis of monodispersed CdSe QD with a narrow size distribution is especially important. To reach this purpose, a lot of methods have been used, including microwave-assisted reduction,[10] wet synthesis at room temperature,[11] photochemical method,[12] colloid method,[13] γ-irradiation[14] and solvothermal methods.[15,16] However, biomimetic and membrane methods have not been reported yet.

In this paper, we have been motivated by the process of refined and adjustable mineralization in biosystem[17] and considered establishing an *in vitro* chemical experimental system to mimic the bioprocess. Here, we adopted a new synthetic method using emulsion liquid membrane (ELM, water-in-oil emulsion with gas as external phase) system[18] to simulate the vesicular structure of biomineralizing units to synthesize CdSe QD. Different from the microemulsion or reverse micelle system, the ELM system has the unique bi-layer membrane structure consisting of membrane solvent, surfactant and carrier. Herein, the membrane is stabilized by surfactant, then the special solute can be actively transferred across the membrane by the carrier. Thus, this intelligent system may imitate the ordered structure of biomembrane and bio-procedure of anti-gradient transport.[19] In order to realize the effective size-control of CdSe QD, different template agents with different concentrations have been introduced into internal phase. It is possible for the method to be applied further in the synthesis of other semiconductor quantum dots.

Experimental

Preparation of emulsion liquid membrane

Into 250 mL of flask, dissolve 3 mL of surfactant (L152) and 5 mL of carrier (N7301) in 42 mL of kerosene, followed by adding 50 mL of 0.1 mol/L $CdCl_2$ solution containing 20% template agent. Agitate for 8—10 min at the rate of 3000 r/min. The ELM system was formed.

Preparation of H_2Se gas and synthesis of CdSe QD

Appropriate amounts of selenium powder and potassium borohydride powder were put into a three-necked flask. In its different mouths a separating funnel, an inlet device for nitrogen gas and an outlet device for H_2Se were respectively installed. Then 100 mL of emulsion

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liquid membrane was sealed in two conical flasks to comprise a set of absorbing system. With the protection of N_2, a dilute solution of HCl (about pH=4) from separating funnel was dropped into three-necked flask at the rate of 1 mL/min under magnetic agitation, and the N_2 carried H_2Se gas into the absorbing system. After selenium powder was dissolved, the reaction was kept for 10 min and the products were formed, then the absorbing system was closed up. The device is shown in Figure 1.

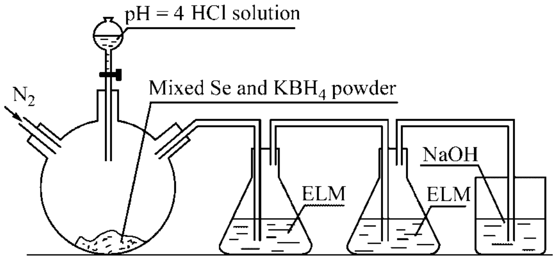

Figure 1 Experimental device for the synthesis of CdSe QD.

The emulsion liquid membrane was demulsified by centrifuge. The obtained precipitate was washed 2—3 times subsequently with dimethylbenzene and absolute ethanol to remove organic impurities. The sample was kept in absolute ethanol.

Characterization of CdSe QD

X-ray diffraction (XRD) was carried out on a Philips Pw1700 X-ray diffractometer, with Cu Kα radiation ($\lambda = 0.15406$ nm). Transmission electron microscopy (TEM) images were taken on a Philips EM400ST transmission electron microscopy, using an accelerating voltage of 100 kV. The ultraviolet-visible (UV-vis) spectrum was measured on an Agilent 8453 instrument. The photoluminescent (PL) spectrum was recorded on a Varian Cary Eclipse instrument.

Results and discussion

Design of the experiment

The design of the proposed method is as follows. (1) Selenium powder is reduced by potassium borohydride in acid solution under the protection of nitrogen atmosphere. H_2Se gas is made in this process. (2) Organic base is chosen as carrier in emulsion liquid membrane system. Simultaneously, it is used for absorbing H_2Se gas in principle. (3) In internal-aqueous phase, $CdCl_2$ reacts with H_2Se to form CdSe QD under the cooperation of the template agent.

It is known that H_2Se shows acid property and is able to react rapidly with alkaline substances, so we choose organic base N7301 (trialiphatic amine, R_3N, R=C_8—C_{10}) as carrier in emulsion liquid membrane system to absorb H_2Se. The carriers and H_2Se could form complex compounds, which were transported into internal-aqueous phase and form CdSe precipitates with $CdCl_2$. The transported process for the synthesis of CdSe nanomaterials is shown in Figure 2.

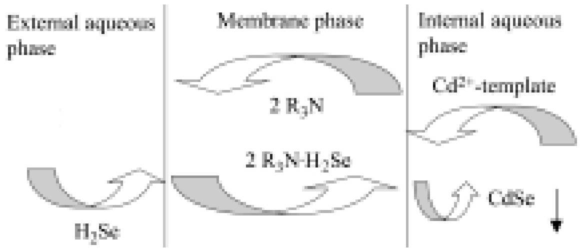

Figure 2 Transport and combination process for forming CdSe QD.

Choices of acidity and instillment rate of acidic solution

As mentioned above, when a dilute solution of HCl in separating funnel is dropped into three-necked flask, selenium powder is reduced by potassium borohydride in the acid solution under the protection of nitrogen atmosphere, and H_2Se gas is formed in this process. The higher the acidity is, the faster the rate of selenium powder reacting with potassium borohydride is. However, when the formed speed of H_2Se is too fast, the emulsion liquid membrane could be destroyed. The experimental results show that the appropriate acidity is pH=4 and corresponding drop rate is 1 mL/min.

Choice of template

With the absence of any additives, disordered CdSe nanoparticles in the size range from 3 to 25 nm were formed. Li *et al.*[20] have reported the preparation of uniform nanocrystalline HgE (E=S, Se, Te) in ethylenediamine (en). So it is feasible to control the size of CdSe QD by the addition of organic template agents. In the present work, three kinds of organic template agents (5-sulfosalicylic acid, sodium citrate and en) were exploited in the internal-aqueous phase. Figure 3 shows the sizes and morphologies of the products obtained in the existence of 20% template agent. When 5-sulfosalicylic acid or sodium citrate was used, well-dispersed CdSe QD with diameters of 3—4 nm was generated (Figures 3a and 3b). When en was used, the as-prepared CdSe particles were also well-dispersed and exhibited spherical shape (Figure 3c). However, their diameters were up to 13—15 nm.

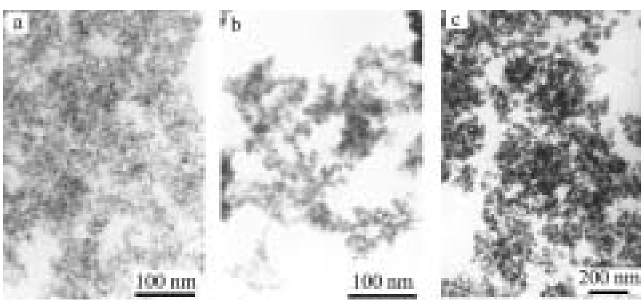

Figure 3 TEM images of CdSe QD: (a) 20% 5-sulfosalicylic acid as the template agent; (b) 20% sodium citrate as the template agent; (c) 20% en as the template agent.

Figure 4 shows the XRD pattern of CdSe QD that was synthesized by using 20% 5-sulfosalicylic acid as the template agent. All the peaks in the pattern can be identified to the known cubic structure of CdSe. The measured lattice parameter is $a=0.6068$ nm, consistent with the reported value $a=0.6077$ nm (JCPDS 19-191).

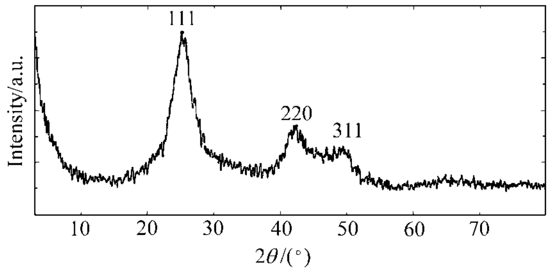

Figure 4 XRD pattern of CdSe QD prepared by using 20% 5-sulfosalicylic acid as the template agent.

Influence of template concentration

The influence of template concentration was also investigated. It is found that the amount of template agents plays a critical role in the size-control of CdSe QD. By increasing the concentration of organic template, smaller particles were generated. The results reveal that the sizes of CdSe particles were up to 9—10 nm when the concentration of 5-sulfosalicylic acid was decreased down to 5%. In the case of using ethylenediamine, similar results can also be obtained, and the sizes of products were decreased down to 10—11 nm when en concentration was up to 40%.

Process of H_2Se transport and CdSe QD formation

The carrier transporting process and CdSe QD forming process are inferred as follows: (1) H_2Se on the interface between external phase and membrane phase forms complex compound with R_3N. (2) The concentration diffusion of the complex compound happens from external interface to internal interface due to its concentration difference between the both interfaces. (3) Cd^{2+}-templates react with $(R_3N)_2{\cdot}H_2Se$ to form CdSe. Subsequently, some CdSe species form crystal nuclei. (4) The CdSe crystal nuclei grow up into CdSe QD by template controlling.

However, the particle size decreases when the concentration of organic template agent is increased. It is probably for increasing the amount of template agent to lead to the existence of great steric hindrances, which preclude the growth of CdSe QD. The transporting and synthetic processes for CdSe nanoparticles have been shown in Figure 2. The chemical equations of the synthetic process (en as the template agent) are listed as follows:

$$Cd^{2+}\ (w) + 2en\ (w) = [Cd(en)_2]^{2+}\ (w) \quad (1)$$

$$4Se\ (s) + KBH_4\ (s) + HCl\ (aq) + 3H_2O = 4H_2Se\ (g) + H_3BO_3\ (aq) + KCl\ (aq) \quad (2)$$

$$H_2Se\ (g) + 2R_3N\ (o) = (R_3N)_2{\cdot}H_2Se\ (o) \quad (3)$$

$$(R_3N)_2{\cdot}H_2Se\ (o) + [Cd(en)_2]^{2+}\ (w) = CdSe\ (w) + 2R_3N\ (o) + 2en\ (w) + 2H^+\ (w) \quad (4)$$

Notes: w, internal aqueous phase; o, organic membrane phase; g, gas; aq, aqueous solution.

Optic properties

Figure 5a gives a UV-vis absorption spectrum of the CdSe QD prepared by using 20% 5-sulfosalicylic acid as the template agent. From the absorption spectrum, we find an observable band at about 545 nm, allowing us to estimate the size of CdSe QD as about 3—4 nm.[21] The obvious blue shift from bulk materials (1.74 eV, 712 nm) may be the reflection of the well-known quantum size effect.

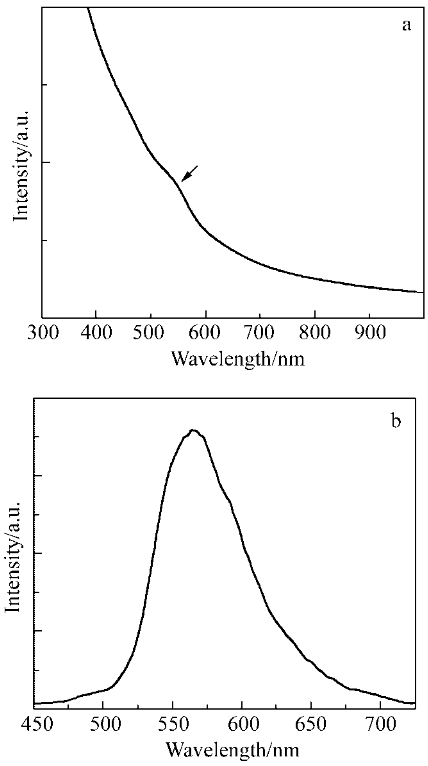

Figure 5 Optic properties of CdSe QD (20% 5-sulfosalicylic acid as template agent). (a) UV-vis spectrum, (b) PL spectrum.

Figure 5b shows a PL spectrum of the synthesized CdSe sample (20% 5-sulfosalicylic acid as template agent). Under excitation at 380 nm, the emission maximum at 565 nm is observed, which has shifted by 20 nm to the red of the absorption spectrum. According to the explanation of Murray *et al.*,[21] this shift is the result of a combination of relaxation into shallow trap state and the size distribution.

Conclusion

In summary, a new biomimetic method based on emulsion liquid membrane system has been developed to synthesize CdSe quantum dots (QD). Various organic template agents with various concentrations are found to effectively control the sizes of the products. Monodispersed CdSe QD with a narrow size distribution of 3—4 nm can be obtained in the presence of 20% 5-sulfosalicylic acid and can show clear quantum size effect. This method provides an *in vitro* biomimetic environment and is possible to be employed to synthesize other novel inorganic nanomaterials in the future.

References

1 Alivisatos, A. P. *Science* **1996**, *271*, 933.

2 Wu, Q. S.; Zheng, N. W.; Ding, Y. P.; Li, Y. D. *Inorg. Chem. Commun.* **2002**, *5*, 671.

3 Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.

4 Zhou, H. C.; Zhuang, J.; Wang, X.; Xu, J.; Li, Y. D. *Acta Chim. Sinica* **2003,** *61*, 372 (in Chinese).

5 Gao, X. H.; Chan, W. C. W.; Nie, S. M. *J. Biomed. Opt.* **2002**, *7*, 532.

6 Chen, Y. F.; Rosenzweig, Z. *Nano Lett.* **2002**, *2*, 1299.

7 Ravindran, S.; Chaudhary, S.; Colburn, B.; Ozkan, M.; Ozkan, C. S. *Nano Lett.* **2003**, *3*, 447.

8 Firth, A. V.; Cole-Hamilton, D. J.; Allen, J. W. *Appl. Phys. Lett.* **1999**, *75*, 3120.

9 Godovsky, D. Y. *Adv. Polym. Sci.* **2000**, *153*, 163.

10 Palchik, O.; Kerner, R.; Gedanken, A.; Weiss, A. M.; Slifkin, M. A.; Palchik, V. *J. Mater. Chem.* **2001**, *11*, 874.

11 Yang, Q.; Tang, K. B.; Wang, C. R.; Zhang, C. J.; Qian, Y. T. *J. Mater. Res.* **2002**, *17*, 1147.

12 Zhao, W. B.; Zhu, J. J.; Chen, H. Y. *J. Cryst. Growth* **2003**, *252*, 587.

13 Chen, Y.; Gao, L. *Chem. Lett.* **2002**, 556.

14 Ge, X. W.; Ni, Y. G.; Liu, H. R.; Ye, Q. G.; Zhang, Z. C. *Mater. Res. Bull.* **2001**, *36*, 1609.

15 Wang, C.; Zhang, W. X.; Qian, X. F.; Zhang, X. M.; Xie, Y.; Qian, Y. T. *Mater. Chem. Phys.* **1999**, *60*, 99.

16 Deng, Z. X.; Li, L. B.; Li, Y. D. *Inorg. Chem.* **2003**, *42*, 2331.

17 Mann, S. *J. Mater. Chem.* **1995**, *5*, 935.

18 Wu, Q. S.; Zheng, N. W.; Li, Y. D.; Ding, Y. P. *J. Membr. Sci.* **2000**, *172*, 199.

19 Voet, D.; Voet, J. G. *Biochemistry*, 2nd ed., John Wiley & Sons, New York, **1995**, p. 525.

20 Li, Y. D.; Ding, Y.; Liao, H.; Qian, Y. T. *J. Phys. Chem. Solids* **1999**, *60*, 965.

21 Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

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