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Assembling Synthesis of ZnSe Orthohexagonal Slices through Emulsion Liquid Membrane System of Gas-liquid Transport

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Abstract: Orthohexagonal slices assembled by ZnSe quantum dots were synthesized through emulsion liquid membrane system. These orthohexagonal slices were 1.5-3.5 μm in side length and were self-assembled by ZnSe quantum dots of 2-3 nm. It was proposed the surfactant molecules on ZnSe quantum dots played a key role in the self-assembly process.

Keywords: ZnSe, emulsion liquid membrane, orthohexagonal slices, self-assembly.

II-VI semiconductor quantum dots (QDs) are ideal materials to be applied in electronics, biology, and so on, because of their unique size-dependent electronic and optical properties[1-3]. However, biomimetic method on synthesis of these QDs has not been reported. Moreover, when we assemble these semiconductor QDs into 2D or 3D nano-assemblies with regular morphologies and novel superlattice structures, it will exhibit potential applications in practical nano-devices based on semiconductor arrays and show important scientific values in structure and morphology[5]. However, up to date, the reports on synthesis of these regular assemblies are still few[5-7].

In this paper, we report a biomimetic and assembling way to synthesize ZnSe QDs and prepare 2D regular orthohexagonal ZnSe slices. In the first stage, ZnSe QDs have been synthesized through emulsion liquid membrane (ELM) system, which is different from well-known microemulsion, by gas-liquid transport. And subsequently, ortho-hexagonal nano-slices are successfully assembled *via* self-organization of surfactant molecules and self-assembly of ZnSe QDs on the basis of their interaction.

Typically, the water-in-oil-in-water (w/o/w) emulsion liquid membrane was prepared in the emulsification step by initially dissolving the surfactant (Span80, 8%) and carrier (N7301, trialiphaticamine R_3N R=C_8-C_{10}, 20%) in the kerosene, then adding 0.1 mol/L $ZnCl_2$ solution. The emulsification was carried out for 8-10 min when agitating at 3000 rpm.

Appropriate amounts of Se powder and KBH_4 powder were put into a three-necked flask, on which a separating funnel, an inlet device for N_2 gas and an outlet device for H_2Se gas were installed. Then 100 mL of emulsion liquid membrane was sealed in a

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conical flask to compose a set of reaction system. With the N_2 protection, a dilute solution of HCl (pH 4) was dropped into the flask at the rate of 2 mL/min under magnetic agitation, and gentle stream N_2 took off H_2Se gas from the reaction system, which was absorbed by NaOH solution. After Se powder was dissolved, the reaction was kept for 10 min and then ceased.

The emulsion liquid membrane was demulsified by centrifuge. The obtained precipitate was washed several times with absolute ethanol until CS determinator (Leco CS-400) showed the surfactant remains were about 0.3-0.4%. The sample was kept in ethanol.

The mechanism of reaction of Se(II) and Zn(II) in ELM is demonstrated as follows.

(1) Se powder is reduced by KBH_4 powder in acid solution under the protection of N_2 atmosphere. H_2Se gas is generated in this step.

(2) As shown in **Figure 1**, organic base N7301 is chosen as carrier in ELM system to form complex compound $(R_3N)_2{\cdot}H_2Se$ with H_2Se. That is to say that with the help of carrier N7301, Se(II) can be transported from external-aqueous phase to internal-aqueous phase.

(3) $ZnCl_2$ in internal-aqueous phase of ELM system reacts with $(R_3N)_2{\cdot}H_2Se$ to obtain ZnSe sample.

In this stage, HCl solution is used to promote the reaction between Se and KBH_4. The faster the HCl solution is dropped into, the faster the output speed of H_2Se is. However, if output speed of H_2Se is too fast, ELM system can be destroyed. The experimental results revealed that the best acidity is pH 4 and addition rate of HCl is 2 mL/min.

An XRD (X-ray diffraction, Philips Pw1700) pattern of the as-prepared sample is shown in **Figure 2**, all the peaks in the pattern can be identified to cubic stilleite structure of ZnSe (PDF 37-1463). The measured lattice parameter is a= 5.715 Å, which is consistent with reported value.

Figure 1 Coupled processes of transporting $(R_3N)_2{\cdot}H_2Se$ and forming ZnSe QDs

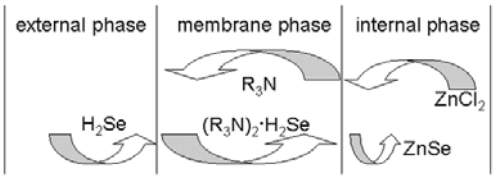


Figure 2 XRD pattern of as-prepared sample

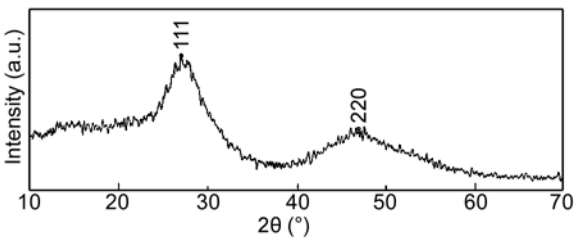
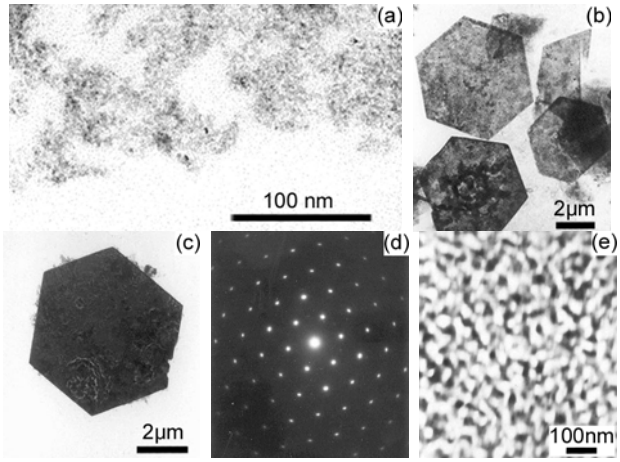


Figure 3 TEM images of as-prepared products



(a) initial ZnSe QDs (b) several orthohexagonal ZnSe slices (c) one orthohexagonal ZnSe slice (d) ED pattern of ZnSe slices (e) high-magnification image of ZnSe slices

Figure 3a shows the TEM (transmission electron microscope, Hitachi H-800) image of fresh products just separated from ELM, indicating the initial as-prepared sample only consists of well dispersed ZnSe QDs with diameters of 2-3 nm. To generate the 2D ZnSe structures, we disperse these QDs adsorbing 0.3-0.4% surfactant in absolute ethanol to form a ZnSe sol, then aging for 24 h. Surprisingly, **Figure 3b** and **3c** reveal that in the final products there are a lot of regular orthohexagonal slices with 1.5-3.5 μm in side length and their thickness are about 10 nm according to semi-transparent appearance and the transmittable result of routine electron-beam, and some unassembled ZnSe QDs still existed. The ED (electron diffraction) pattern (**Figure 3d**) shows single crystalline diffraction dots. To learn more about the microstructure of these slices, magnification TEM image is shown in **Figure 3e**. The self-assembly nature of these ZnSe nanoparticles is obviously observed from the slices assembled regularly by nanoparticles. However, these ZnSe nanoparticles with diameters of 15-30 nm are larger than the initial ZnSe QDs, which implies the self-assembly is multi-step process.

It seems that the formation process of orthohexagonal ZnSe slices is complicated. Nevertheless, it is clear that at least we can divide this process into two main stages: the formation of ZnSe QDs and the self-assembly of ZnSe QDs to orthohexagonal slices. Previously, it has been demonstrated that ELM system is efficient in limiting the particle size in nanometer scale[8,9], attributed to the unique biomimetic double-layer membrane structure and the interaction between original particles and surfactant molecules. So, we are reasonable to depict the first stage of forming ZnSe QDs as follows: (1) H_2Se gas complex with N7301 to form $(R_3N)_2H_2Se$ to be transported into internal-aqueous phase; (2) Zn(II) reacts with Se(II) to form ZnSe nuclei; (3) limited by the ELM system, ZnSe nuclei grow into ZnSe QDs.

In the past decade, organic-inorganic interaction has been emphasized in the generation of novel ordered inorganic materials[10-13] and biomineralization[14]. Recently,

single crystalline porous vaterite hexagonal prisms have been reported through self-oriented attachment of nanoparticles in gelatin[15]. Our contrast experiments also confirmed that orthohexagonl slices cannot form without surfactant. Therefore, obviously, in addition to stabilizing ELM structure, organic additives may play a crucial role in the self-assembly. Here, we speculate the proposed mechanism of self-assembly of ZnSe QDs: (1) the remnant surfactant on ZnSe QDs dissolved gradually in ethanol, then ZnSe QDs grow into nanoparticles of 15-30 nm to reduce surface energy; (2) according to widely accepted micelle theory[16], surfactant molecules self-organize into hexagonal liquid crystalline template through interaction with ZnSe nanoparticles in ethanol; (3) at the same time, ZnSe nanoparticles self-assemble into orthohexagonal slices under direction of surfactant liquid crystalline template.

In summary, ZnSe QDs and 2D orthohexagonal ZnSe slices have been obtained through ELM system. The overall mechanism is preliminarily discussed, multi-step self-assembly of initial ZnSe QDs may account for the formation of final regular slices. This method may be promising in preparation of novel 2D nano-structures and future nano-device based on these structures.

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