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High quantum yield ZnO quantum dots synthesizing via an ultrasonication microreactor method

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ABSTRACT

Green emission ZnO quantum dots were synthesized by an ultrasonic microreactor. Ultrasonic radiation brought bubbles through ultrasonic cavitation. These bubbles built microreactor inside the microreactor. The photoluminescence properties of ZnO quantum dots synthesized with different flow rate, ultrasonic power and temperature were discussed. Flow rate, ultrasonic power and temperature would influence the type and quantity of defects in ZnO quantum dots. The sizes of ZnO quantum dots would be controlled by those conditions as well. Flow rate affected the reaction time. With the increasing of flow rate, the sizes of ZnO quantum dots decreased and the quantum yields first increased then decreased. Ultrasonic power changed the ultrasonic cavitation intensity, which affected the reaction energy and the separation of the solution. With the increasing of ultrasonic power, sizes of ZnO quantum dots first decreased then increased, while the quantum yields kept increasing. The effect of ultrasonic temperature on the photoluminescence properties of ZnO quantum dots was influenced by the flow rate. Different flow rate related to opposite changing trend. Moreover, the quantum yields of ZnO QDs synthesized by ultrasonic microreactor could reach 64.7%, which is higher than those synthesized only under ultrasonic radiation or only by microreactor.

1. Introduction

Colloid quantum dots (QDs) attracted much attention in recent years due to their amazing characteristics in optics. It is easy to adjust the energy gap of QDs by changing the size of QDs. The sizes of QDs could be controlled by the synthesis methods. Zinc oxide (ZnO) QDs exhibits excellent UV-absorption and photoluminescence properties due to the wide band gap (3.37 eV) and large excitation binding energy (60 meV) [1,2]. Colloid ZnO QDs would be used in vivo imaging because of the hypotoxicity [3]. Whereas it is not easy to synthesize high optical quality ZnO QDs with uniform sizes and less surface defects by the conventional sol–gel method.

Microreactor has been used to synthesize organics for a long time. Nowadays, it is also employed to synthesize the nanoparticles [4–7]. The advantages of microreactor include quick heat and mass transferring, high speed mixing, precise and controllable feeding, easy and stable industrial experimenting [8]. Microreactor could be classified into reverse micelle microreactor, membrane dispersion microreactor, continuous flow microreactor and so on. Compared with other microreactors, continuous flow microreactor is easy to build. However, as the reaction solution is continuous flowing in the tube, the microreactor could be more micro. Introducing the second phase is a helpful way [4]. But for the reaction in alcohol, it is hard to create second phase through conventional method.

Reactions under ultrasonic radiation have different processes [9–11]. Ultrasonic radiation brings more free radicals in the system [12], enhanced the energy of the reaction system and improved the reaction activity of the reactant. Ultrasonic radiation can also control the morphology and reduce the surface defects of QDs [13]. Furthermore, due to the ultrasonic cavitation, ultrasonic radiation would easily create bubbles in the solution. This could be a simple way to create a second phase in the continuous flow microreactor.

There are some researches on ultrasonic method [14,15] and microreactor method [16–18] respectively. Even some researchers have employed ultrasonic microreactor to synthesize materials

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[19,20], there is still little research on the ultrasonic effect on microreactor. In this article, the ultrasonic method and microreactor method were combined as an ultrasonic microreactor method to synthesize ZnO QDs. The effects of flow rate, ultrasonic power and temperature on the photoluminescence properties of ZnO QDs were explored. The reaction mechanisms were discussed as well.

2. Material and methods

2.1. Materials

Ethyl alcohol (99.7%), polyethylene glycol-400 (PEG-400, 99.0%), lithium hydroxide ($LiOH{\cdot}H_2O$, 95.0%), oleic acid (OA, 99.0%), *n*-hexane (97.0%) from Shanghai Lingfeng Chemical company and zinc acetate ($Zn(Ac)_2{\cdot}2H_2O$, 99.0%) from Xilong Chemical company have been used without further purification.

2.2. Synthesis of ZnO QDs by ultrasonic microreactor method

ZnO QDs samples were prepared via an ultrasonic microreactor method [10,16,21,22]. The experimental setup is displayed in Fig. 1. $Zn(Ac)_2$ ethanolic solution of 0.05 mol/L was prepared by dissolving 0.55 g (0.0025 mol) $Zn(Ac)_2{\cdot}2H_2O$ and PEG-400 with *n*(PEG): *n*(Zn) = 1:1 in 50 mL ethyl alcohol. LiOH ethanolic solution of 0.1 mol/L was prepared by dissolving 0.21 g (0.005 mol) $LiOH{\cdot}H_2O$ in 50 mL ethyl alcohol. Both $Zn(Ac)_2$ solution and LiOH solution were dissolved under ultrasonic radiation at 40 °C for 10 min. After the solutions became clear, two injectors were employed to inhale 30 mL $Zn(Ac)_2$ solution and 30 mL LiOH solution respectively. The solutions were injected into PTFE tube (inner diameter: Φ = 0.8 mm, length = 1.5 m) by the double syringe pump and mixed through a "Y" shape micromixer with total interior volume of about 10 μL. The PTFE tube was immersed in an ultrasonic washer, which provided ultrasonic radiation (ultrasonic frequency = 53 kHz, ultrasonic power = 0 W, 72 W to 180 W). The reaction temperatures between 20 °C and 60 °C were exactly controlled by a low temperature thermostat. Flow rates were changed from 150 μL/min to 900 μL/min to change the reaction time. ZnO QDs were collected in an erlenmeyer flask, and 0.6 mL oleic acid (OA) was used to precipitate the QDs. The white sediment was isolated by centrifugation for 5 min under 4000 r/min and washed for 2–3 times with excess ethanol to remove any un-reacted material. Finally, ZnO QDs were dispersed in the *n*-hexane for further measurement.

2.3. Measurement

The photoluminescence spectra was measured using a fluorescent spectrophotometer (Lumina, Thermo, USA). For each sample, the emission spectrum was taken under the measured emission peak as the excitation wavelength. The excitation spectrum was taken under the measured emission peak as the emission wavelength. The absorption spectra were recorded on a UV–Vis–NIR spectrophotometer (UV-3600, Shimadzu, Japan) employed *n*-hexane as a reference. The TEM micrographs were characterized by transmission electron microscopy (JEM-2100, JOEL, Japan).

The photoluminescence quantum yields (PL QYs) were calculated by the following equation, using Rhodamine 6G dissolved in water (QY = 95%) as Ref. [16]:

$$QY_{sample} = \left(\frac{F_{sample}}{F_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right)QY_{ref} \quad (1)$$

where *F* is the measured fluorescence, *A* is the absorbance at the excitation wavelength, and n is the refractive index of the solvent.

3. Results and discussion

3.1. Flow rate of reaction

The formation of ZnO nanostructures was reported to be [23]:

$$Zn^{2+} + 4OH^- \longrightarrow Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{2-} \longrightarrow ZnO_2^{2-} + 2H_2O \quad (3)$$

$$ZnO_2^{2-} + H_2O \longrightarrow ZnO + 2OH^- \quad (4)$$

$$ZnO + OH^- \longrightarrow ZnOOH^- \quad (5)$$

Fig. 2(a) displays the UV–Vis absorption spectra of ZnO QDs synthesized in 40 °C with 0 W ultrasonic power under different flow rate. All the samples absorption start from about 350 nm. The 99% absorption wavelength decreased from 348 nm to 344 nm with the increasing of flow rate.

The optical gap E_{gap} of ZnO QDs could be calculated by Formula (6) [24]:

$$\alpha = \frac{A(h\nu - E_{gap})^n}{h\nu} \quad (6)$$

where α is the absorption coefficient proportional to the absorbance, *A* is a constant and *n* is a constant equal to 1/2 for direct gap semiconductors and 2 for indirect gap semiconductors [25,26]. As ZnO is a direct gap semiconductor [27,28], this formula

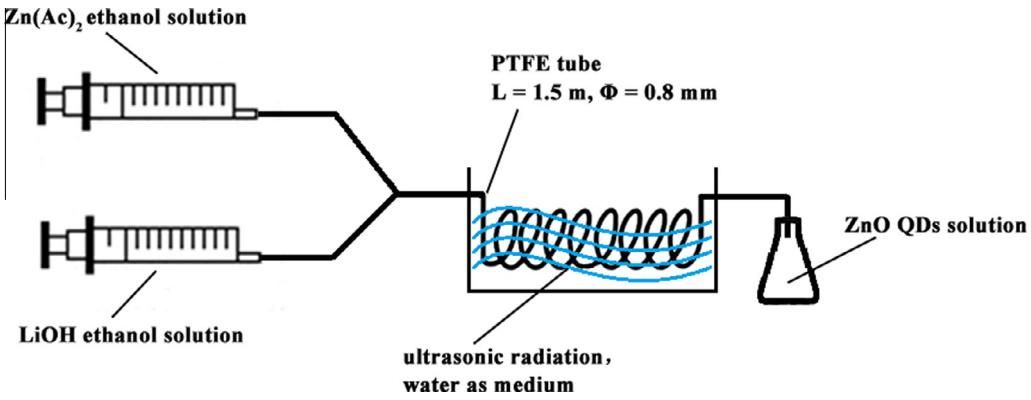

Fig. 1. Experimental setup of ultrasonic microreactor.