Research Article

Xilian Zhang, Shanshan Luo, Xiaodan Wu, Minghui Feng, Yingying Li, Haoyun Han, Wenkui Li*

Effect of alkali bases on the synthesis of ZnO quantum dots

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Abstract: The surface-modified zinc oxide quantum dots (ZnO QDs) have broad application prospects in the field of biomedicine because of their good water solubility, dispersibility, and high fluorescence stability. The alkali bases play important roles in controlling the morphology, size distribution, dispersity, and fluorescence intensity of the synthesized ZnO QDs. In this article, ZnO QDs were synthesized to induce hydrolysis–condensation reaction. The influences of alkali bases (LiOH, NaOH, and KOH) and the ratio of $n(\text{Zn}^{2+}):n(\text{OH}^-)$ on the properties of synthesized ZnO QDs were investigated. The results show that the particle size of the ZnO QDs prepared using LiOH and NaOH as raw materials are smaller than that using KOH. ZnO QDs prepared at the ratio of $n(\text{Zn}^{2+}):n(\text{LiOH}) = 1:1$ have the best fluorescence performance and dispersibility.

Keywords: zinc oxide, quantum dots, alkaline, fluorescence properties, water solubility

1 Introduction

Quantum dots (QDs) are semiconductor materials with a particle size close to or smaller than the de Broglie wave or the mean free path of electrons. During the past few

decades, QDs have been widely studied because of their adjustable size and luminescent properties that make them promising agents for biomedicine [1,2], information encryption [3], and optoelectronic devices. Applications in the biomedical field require ZnO QDs to have good water solubility, dispersion, and fluorescence stability.

The fluorescence color of the QDs is related to their size. In the range of 2.5–7 nm, as the particle size increases, the fluorescence color is blue-violet, blue, green, yellow, orange, and red [4,5]. In 1991, Lubomir and Marc [6] prepared ZnO QDs with a size of 3–6 nm for the first time using zinc acetate and LiOH as the starting materials through a sol–gel method. Also, various methods have been used to prepare ZnO QDs, including the sol–gel method [7–9], the microemulsion method [10–12], the hydrothermal method [13,14], and so on. The sol–gel method is widely used in the laboratory research for its convenience of doping and controllability of reaction conditions. However, colloidal ZnO QDs are easy to aggregate or undergo Ostwald ripening because of their high surface energy. As a result, ZnO QDs are unstable in the aqueous dispersion used for storage. [15]. To stabilize ZnO QDs, various capping agents have been used, i.e., polyvinylpyrrolidone, 3-aminopropyltrimethoxysilane (APTES), amines, mercaptocarboxylic acid, etc. [16,17]. The alkoxy groups in APTES hydrolyze and react with the –OH group on the surface of the ZnO to form a silica capping layer. In addition to being a biocompatible molecule, silica serves two more important functions, namely, controlling the particle size by limiting the growth of ZnO and acting as a side group on the surface that can be further conjugated with biomolecules [18]. In the sol–gel method, various factors, including doping, the concentration of precursor, the reaction temperature, and the molar ratio of the reactants, affect the final performance of the synthesized ZnO QDs. A small amount of Mg^{2+} doping (<10%) can significantly improve the fluorescence performance [19] and prevent the agglomeration of ZnO QDs [20]. A high concentration of zinc acetate and prolonged reaction time are beneficial for the growth of the ZnO particles [21].

* **Corresponding author: Wenkui Li**, Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China, e-mail: liwenkui1976@163.com

Xilian Zhang: Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China

Shanshan Luo, Minghui Feng, Yingying Li, Haoyun Han: Jiangxi Provincial Key Laboratory of Drug Design and Evaluation, School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China

Xiaodan Wu: State Key Laboratory of Food Science and MOE Biomass Energy Center, Nanchang University, Nanchang 330013, People's Republic of China

Various research studies have been reported on the synthesis of ZnO nanomaterials with the controlled crystal size and the surface structure to improve their properties for a potential application. Few studies have focused on the influence of the alkali base types on the size and morphology tunability of ZnO nanomaterials [22,23]. However, there is no report on the effect of alkali base types on the dispersibility of water-soluble ZnO QDs as far as we know. Moreover, the results over the ratio of hydroxide to zinc ions on the fluorescence properties of QDs are controversial [21,24]. In this study, ZnO QDs were prepared by the sol-gel method, and their surface was modified by APTES to make them water soluble. The effects of the different alkali bases (LiOH, NaOH, and KOH) and $R_{\text{Zn-OH}}$, which is the ratio of $n(\text{Zn}^{2+}):n(\text{OH}^-)$, on the size, dispersibility, and fluorescence properties of ZnO QDs were studied.

2 Materials and methods

2.1 Materials

Zinc acetate dihydrate, magnesium acetate tetrahydrate, potassium hydroxide (Shanghai Titan Technology Co., Ltd.), sodium hydroxide (Guangdong West Long Science Co., Ltd.), lithium hydroxide (Shanghai Aladdin Biochemical Technology Co., Ltd.), 3-aminopropyltriethoxysilane (Shanghai Yien Chemical Technology Co., Ltd.), ethanol, and *n*-hexane (China National Pharmaceutical Group Shanghai Chemical Reagent Company) were used in this study. All the reagents used in this study are of analytical grade and were used without further purification.

2.2 Preparation of ZnO QDs

The water-soluble ZnO QDs were prepared according to the sol-gel method [19] with a small modification. A typical two-step synthesis route is shown in Figure 1 and described as follows: in the first step, 2.20 g zinc acetate dihydrate and 0.214 g magnesium acetate tetrahydrate were dissolved in 100 mL of anhydrous ethanol, and then, the solution was refluxed and stirred for 150 min at 80°C in a water bath until the solution became colorless and transparent. Then, the solution was placed in an ice bath. LiOH, NaOH, or KOH was weighed and dissolved in 150 mL of absolute ethanol, according to $R_{\text{Zn-OH}} = 1:1$ and 1:2, and then heated and stirred at

Figure 1: A typical routing of preparing ZnO QDs by the sol-gel method.

85°C until the solution became colorless and transparent, and then the solution is cooled to room temperature and added to the ethanol solution of zinc acetate in an ice bath and reacted for 4 h. The solution quickly turned white and then gradually became clear, indicating that ZnO QDs were formed. In the second step, 400 μL of APTES solution was mixed with 2 mL of ultrapure water, and then, the mixed solution was added dropwise to the aforementioned ZnO QD solution, and the mixed solution was stirred at 60°C for 3 h. APTES undergoes hydrolysis to form silica-coated ZnO QDs. As the reaction completed, white ZnO QD precipitates were centrifuged at 4,500 rpm for 5 min, followed by washing twice with ethanol to remove unreacted impurities and finally vacuum dried at 60°C to obtain ZnO QD powders.

2.3 Characteristics

The crystal structure and composition were measured through an X-ray powder diffractometer (Shimadzu, Japan, XRD-6100). The morphology and particle size were observed using a field emission transmission electron microscope (FEI Company, USA). Surface functional groups were determined using a Fourier transform infrared spectrometer (IR-960, Tianjin Rui'an Technology Co., Ltd.). The fluorescence performance was tested by a UV spectrophotometer (model UV-2550, Shimadzu, Japan), a PL fluorescence spectroscopy (Beijing Zhuoli Hanguang Instrument Co., Ltd.), and a fluorescence spectrometer (Hitachi High-Tech Co., Ltd., Japan).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

In the XRD spectrum of ZnO QDs (as shown in Figure 2), the characteristic peaks of ZnO (100), (002), (101), (102), (110), (103), and (112) are all consistent with the standard card JCPDS (99-0111), indicating that the crystal structure of the synthesized ZnO QDs is wurtzite. Because of the small particle size of ZnO QDs, the half-width of the diffraction peak is broadened. The half-width of the diffraction peak of the sample with $R_{\text{Zn-OH}} = 1:2$ is larger than that of the sample with $R_{\text{Zn-OH}} = 1:1$, which indicates that the particle size of the QDs prepared at $R_{\text{Zn-OH}} = 1:2$ is smaller than that prepared at $R_{\text{Zn-OH}} = 1:1$. When $R_{\text{Zn-OH}}$ is fixed at 1:1, the ZnO QDs synthesized with LiOH are the smallest.

Figure 3 shows the TEM results of each sample. The particle size of the ZnO QDs prepared at $R_{\text{Zn-OH}} = 1:2$ is smaller than that prepared at $R_{\text{Zn-OH}} = 1:1$. The morphology of the QDs with $R_{\text{Zn-OH}} = 1:1$ shows better uniformity. Regardless of $R_{\text{Zn-OH}}$, the dispersion of ZnO QDs prepared with LiOH as the alkali base is better than that prepared with NaOH and KOH. This may be due to the different dissociation constants of the alkali base ($K_{\text{D}}^{\text{LiOH}} < K_{\text{D}}^{\text{NaOH}} < K_{\text{D}}^{\text{KOH}}$) [25]. As the synthesis process of the QDs is a relatively violent reaction process, a low dissociation constant is beneficial to the formation of uniform particle morphology. The selected area electron diffraction pattern (SAED) shows that the ZnO QDs with $R_{\text{Zn-OH}} = 1:1$ has better crystallinity than that with $R_{\text{Zn-OH}} = 1:2$.

Figure 4 shows the HRTEM and diffraction ring of ZnO QDs prepared with $R_{\text{Zn-OH}} = 1:1$ using LiOH as the alkali base. Each crystal plane corresponds to the crystal

plane in the XRD diagram, and the average particle size is about 5.5 nm, with a uniform distribution.

The presence of silica capping has been explained from the FTIR studies on the samples. To explore the functional groups on the surface of the ZnO QDs, infrared characterization was used as shown in Figure 5. The observation of an absorption peak at 900 cm^{-1} , corresponding to Si–O vibration, suggests the presence of silica in the capped ZnO QDs. The sketch of the silanization method is shown in Figure 6. In the sample of uncapped ZnO QDs, an absorption peak is observed at 470 cm^{-1} , corresponding to the Zn–O stretching vibrations. Furthermore, this peak is found to be shifted to the lower wave number 456, 450, and 443 cm^{-1} for samples. The shift of Zn–O peak in all the capped samples has been found unidirectional toward the lower wave number side, which is indicative of an increase in the effective mass of the Zn–O system [18]. The absorption peak at $3,420 \text{ cm}^{-1}$ is because of the O–H stretching vibrations. However, compared with the samples of $R_{\text{Zn-OH}} = 1:1$, there is no N–H stretching vibration peak in the range of $3,000\text{--}3,500 \text{ cm}^{-1}$ with the samples of $R_{\text{Zn-OH}} = 1:2$. They are derived from the N–H and O–H stretching vibration absorption peaks. The peak at $1,420 \text{ cm}^{-1}$ is the flexural vibration absorption peak of C–H, and the peak at $1,580 \text{ cm}^{-1}$ is the flexural vibration absorption peak of the end group --NH_2 . The IR spectrum proves that there are hydroxyl and amino functional groups on the surface of the ZnO QDs. It shows that the high content of OH^- is harmful to the hydrolysis of APTES to form silica, so the content of the modified functional groups on the surface of the ZnO QDs prepared with $R_{\text{Zn-OH}} = 1:2$ is less. The hydroxyl and amino functional groups are hydrophilic groups, which enhance the stability and solubility of the ZnO QDs in water.

Figure 7 shows the ultraviolet-visible absorption spectrum of ZnO QDs. All the ZnO QDs have exciton absorption peaks because of the relatively larger binding energy of the exciton (60 mV) [26]. The UV absorption edge of the samples of $R_{\text{Zn-OH}} = 1:2$ has a more significant blueshift than the samples of $R_{\text{Zn-OH}} = 1:1$. The blueshift is caused by the quantum size effect. The blueshift is more obvious with a decrease in the particle size. Therefore, it can be inferred that the particle size of the ZnO QDs prepared with $R_{\text{Zn-OH}} = 1:2$ is relatively smaller, which is consistent with the results of XRD and TEM. $R_{\text{Zn-OH}}$ has a significant effect on the UV absorption intensity of ZnO QDs. Samples with $R_{\text{Zn-OH}} = 1:1$ has a stronger absorption than those with $R_{\text{Zn-OH}} = 1:2$, which is consistent with the results of the infrared spectrum. The ultraviolet-visible absorption of ZnO QDs is related to the band gap energy.

Figure 2: XRD pattern of ZnO QDs synthesized under different alkali bases and $R_{\text{Zn-OH}}$ values.

Figure 3: TEM image and SAED image of ZnO QDs synthesized with different alkali bases and $R_{\text{Zn-OH}}$ values.

Figure 4: HRTEM image, SAED image, and particle size distribution image of ZnO QDs synthesized at $R_{\text{Zn-LiOH}} = 1:1$.

Because of the quantum size effect of ZnO QDs, the band gap energy increases with the decrease in the size, and the absorption edge is blue shifted in the ultraviolet-visible absorption spectrum. The difference in absorbance is because the water solubility of $R_{\text{Zn:OH}} = 1:1$ is better than that of $R_{\text{Zn:OH}} = 1:2$, and the content in the solution is higher, so the absorbance is relatively larger.

Figure 8 shows ZnO QDs (LiOH , $R_{\text{Zn-OH}} = 1:1$) solid powder under 365 nm UV lighting and visible light, which shows that ZnO QDs emit a strong yellow fluorescence under UV lighting. The solid-state fluorescence spectrum of ZnO QDs (EX = 324 nm) is shown in Figure 8. There are two fluorescence emission peaks in the spectrum, namely, a weak and sharp ultraviolet emission peak

Figure 5: IR spectra of ZnO QDs synthesized with different alkali bases and different R_{Zn-OH} values.

Figure 6: Sketch of the silanization method.

Figure 7: Ultraviolet-visible spectra of ZnO QDs synthesized under different alkali bases and different R_{Zn-OH} values.

(370 nm) and a strong and broad yellow emission peak (530 nm). It is well known that the intensity of emission depends on both size and surface properties of the dots.

Silica coated with ZnO QDs usually does not affect the absorption and luminescence properties of the semiconductor nanoparticles, exhibiting good optical transparency [27]. The luminescence peak at 370 nm is generated by exciton recombination [28,29], which is caused by the transition of electrons from the bottom of the conduction band of ZnO to the valence band, which constitutes the inherent fluorescence of the material. Several studies have been reported to explain the origin of broad emission from ZnO in the visible region [30–32]. It is reported that this band is an envelope spectrum of multiple emission bands originating from different defect centers such as zinc vacancy (V_{Zn}), zinc interstitial (Zn_i), oxygen vacancy (V_o^+), oxygen interstitial (O_i), and antisite oxygen (O_{Zn}). Dijken et al. [32] suggested that the visible emission from nanocrystalline ZnO particles is because of the transition of a photogenerated electron from the conduction band to a deeply trapped hole (V_o^{++}). The visible emission maxima at 530 nm of different sized ZnO QDs observed in the present studies can also be assigned to the transition of photogenerated electrons from the conduction band edge to a deeply trapped level (V_o^{++} centers).

Figure 8: Solid-state fluorescence spectra of ZnO QDs synthesized under different alkali bases and different $R_{\text{Zn-OH}} = 1:1$ (a), $R_{\text{Zn-OH}} = 1:2$ (b), and fluorescence of different alkaline and $R_{\text{Zn-OH}}$ ratios under UV irradiation (c and d).

The specific luminescence transition mechanism diagram is shown in Figure 9. The luminescence performance is also related to the preparation method and react parameters, so further deep research studies are needed. Regardless of the alkali base, the luminescence intensity of ZnO QDs at $R_{\text{Zn-OH}} = 1:2$ is stronger than that at $R_{\text{Zn-OH}} = 1:1$ in the range of 500–530 nm, indicating that the defect concentration of ZnO QDs prepared at $R_{\text{Zn-OH}} = 1:2$ is high. This indicates that the hydrolysis reaction of APTES is inhibited under the condition of $R_{\text{Zn-OH}} = 1:2$, resulting in an incomplete silica covering layer and numerous surface defects on the surface of the QDs.

Figure 10 shows the difference between the liquid fluorescence spectrum of ZnO QDs (EX = 350 nm) and the solid fluorescence spectrum of ZnO QDs (EX = 324 nm). In the

Figure 9: Schematic diagram of luminescence mechanism of QDs.

aqueous solution, the ZnO QDs prepared with $R_{\text{Zn-OH}} = 1:2$ have almost no fluorescence emission because of its poor water solubility. The ZnO QDs prepared with $R_{\text{Zn-OH}} = 1:1$ show a yellow emission peak at about 570 nm. It is different from the yellow fluorescence emission position measured in solids because aging caused the peak shift [7]. The digital photos are ZnO QDs dispersed in the ultrapure water under 365 nm UV light. It can be seen that the ZnO QDs prepared at $R_{\text{Zn-OH}} = 1:1$ emit very strong yellow light, whereas the samples prepared at $R_{\text{Zn-OH}} = 1:2$ hardly emit light.

The growth of the ZnO QDs is first through the directional attachment and bonding mechanism, and then the maturation and coarsening of Ostwald ripening [33]. But when the alkali base is KOH, it will experience the third type: secondary precipitation of ZnO QDs, which makes the particles larger. Currently, the formation mechanism of ZnO QDs is still unclear, and the different processes have been proposed because of the difference in the intermediate substances [34]. The most common nucleation and growth mechanism of ZnO QDs were proposed by Jun *et al.* [9]. The specific reaction is as follows:

where $(\text{ZnO})_n$ represents the crystal nucleus, and $(\text{ZnO})_{n+k}$ represents the QD grown from the crystal nucleus. Equation (1) indicates that the reaction occurs when Zn^{2+} and OH^- mix, then generating $[\text{Zn}(\text{OH})]^+$. Equations (2) and (3) represent nucleation and growth, respectively. Only when the $[\text{Zn}(\text{OH})]^+$ concentration reaches a certain value, the reaction in equation (2) can be triggered. Once equation (2) is triggered, the reaction in equation (3) will proceed simultaneously.

The alkali bases have different dissociation constants ($K_D^{\text{LiOH}} < K_D^{\text{NaOH}} < K_D^{\text{KOH}}$), which affect the content of OH^- . When the $R_{\text{Zn-OH}}$ is kept as a constant, low dissociation constants result in small reaction driving force, which reduces the growth efficiency of ZnO QD, and the particles are relatively dispersible. The difference in yield also follows the order of dissociation constants of LiOH, NaOH, and KOH. The smaller the number of QDs generated at the same time, the less agglomeration formed to a certain extent.

4 Conclusions

ZnO QDs have a potential application in the medical fields, but the preparation of high-quality ZnO QDs is still

Figure 10: Liquid-state fluorescence spectra of ZnO QDs synthesized under different alkali bases and different $R_{\text{Zn-OH}}$ values (a). Images of the ZnO QDs under UV lighting and white lighting conditions (b and c).

a challenge. The alkali bases and $R_{\text{Zn-OH}}$ are vital factors influencing the morphology and performance of ZnO QDs in the sol-gel method. This article studies the influence of the ratio of different alkali bases (LiOH, NaOH, and KOH) and $R_{\text{Zn-OH}}$ on the performance of ZnO QDs. The results show that ZnO QDs can be synthesized successfully using any one of the three alkali bases, and higher OH^- concentration is beneficial for forming a smaller particle size, but harmful for the water solubility and the fluorescence intensity. The difference in dissociation constants may be the major reason that influences the reaction process. The particle size of the ZnO QDs prepared using LiOH and NaOH as raw materials is smaller than that prepared using KOH. ZnO QDs prepared at the ratio of $n(\text{Zn}^{2+}):n(\text{LiOH}) = 1:1$ have the best fluorescence performance and dispersibility.

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