SPECIAL TOPIC — Physical research in liquid crystal

Synthesis of ZnO quantum dots and their agglomeration mechanisms along with emission spectra based on ageing time and temperature*

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The ZnO quantum dots (QDs) were synthesized with improved chemical solution method. The size of the ZnO QDs is exceedingly uniform with a diameter of approximately 4.8 nm, which are homogeneously dispersed in ethanol. The optical absorption edge shifts from 370 nm of bulk material to 359 nm of QD materials due to the quantum size effect, while the photoluminescence peak shifts from 375 nm to 387 nm with the increase of the density of ZnO QDs. The stability of ZnO QDs was studied with different dispersion degrees at 0 °C and at room temperature of 25 °C. The agglomeration mechanisms and their relationship with the emission spectra were uncovered for the first time. With the ageing of ZnO QDs, the agglomeration is aggravated and the surface defects increase, which leads to the defect emission.

Keywords: ZnO quantum dots, quantum blue shift, agglomeration mechanism, stability

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1. Introduction

In recent years, low-cost solution-based synthesis of colloidal semiconductor quantum dots (QDs) have drawn increasing attention due to their applications on quantum dots-based LEDs which exhibit highly pure and saturated color gamut,[1,2] narrow-band width QD photodetectors,[3] and single-electron transistors.[4] Quantum dots have such advantages as color tunableness, high solution processability and high color purity. The size of QDs can be controlled to adjust the emission color with the same chemical composition. However, the stability of QDs becomes a technology bottleneck which restricts their development and applications. The agglomeration and water-oxygen reaction are two key factors that affect the stability of QDs.

ZnO quantum dots with a direct wide bandgap of 3.37 eV have been extensively investigated by many researchers over the last decades.[5] Meanwhile, CdSe/CdS family quantum dots[6,7] and inorganic perovskite $CsPbX_3$ family quantum dots[8,9] boom with high potential interest on optoelectronic devices in recent years. When the scale of at least one dimension is below approximately 7 nm, the quantum size effect starts to dominate the material system.[10] Nevertheless, QD materials have less defects inside the materials but massive defects or dangling bonds at the surface due to their high specific surface area, which further generate agglomeration facilely.

In this paper, ZnO QDs have been prepared and investigated while the agglomeration mechanisms of QDs and their relationship with the emission spectra are uncovered for the first time.

2. Experimental sections

The zinc precursor was prepared by refluxing ethanolic solution containing zinc acetate of 0.1 mol for 2–3 h. Next, 10 mL of zinc complex precursor solution was diluted to 20 mL with ethanol. Then, 117 mg (2.8 mmol) of LiOH powder was added to the diluted ethanolic solution. Finally, the ZnO QDs were obtained at constant temperature. In order to purify the ZnO QDs, the ZnO QDs were washed twice by precipitation with n-hexane and dissolution in ethanol for removing excess Zn^{2+} and Li^{+} ions.

The crystal structure of the ZnO QD powders was analyzed by x-ray diffraction (XRD, Y-2000X), operated at 45 kV and 40 mA using Ni-filtered Cu K_α radiation with a scan speed of 10°/min for 2θ in a range from 20° to 80°. The morphology and size of the sample were observed by transmission electron microscope (TEM) using an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Characterization of ZnO quantum dots

The x-ray diffraction (XRD) pattern of ZnO QDs is shown in Fig. 1, which reveals that the QDs are ZnO with a hexagonal wurtzite crystal structure (according to ZnO JCPDS in Fig. 1), with an approximate diameter of 4.8 nm which is estimated according to Scherrer's formula

$$D_c = 0.89\lambda/(B\cos\theta), \quad (1)$$

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where B is the half-peak width. The λ in the XRD measurement is 0.154178 nm under $K\alpha$ radiation of Ni-filtered Cu target. The θ is from 20° to 80°.

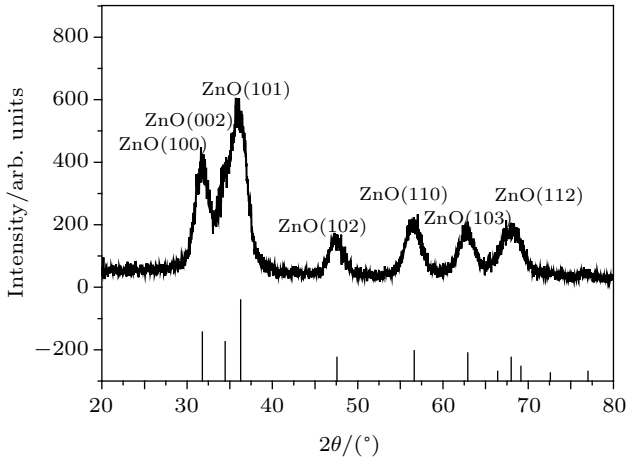


Fig. 1. X-ray diffraction spectrum of ZnO quantum dots.

It is shown in Fig. 2 that the ZnO QDs demonstrate high dispersion, high homogeneity dimensional, with an approximate diameter of 4.8 nm, which is absolutely the same as estimation by Scherrer's formula. The lattice constant of hexagonal wurtzite crystal structure of ZnO can also be verified in the magnified TEM images with the distance of crystal faces $a = 0.3$ nm and $c = 0.5$ nm as the hexagonal crystal structure. It infers that the QDs are synthetic with good crystallinity.

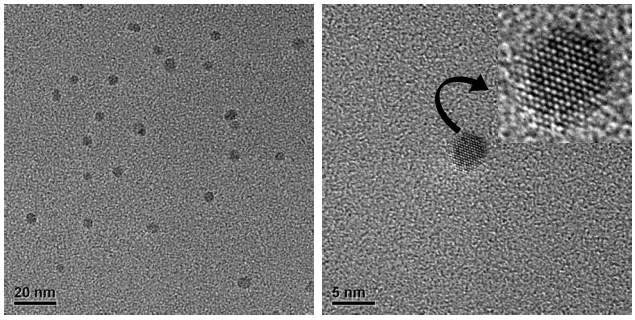


Fig. 2. TEM images of ZnO quantum dots.

3.2. Photoluminescence resolved with density of ZnO QDs

The absorbance spectra and photoluminescence spectra of the hybrid ZnO QDs are randomly distributed in the ethanol as shown in Fig. 3. The optical absorbance spectrum of ethanol is chosen as a reference background, which has been subtracted from the spectrum to remove the effects of the substrate. The absorption edge at 359 nm is attributed to the ZnO QDs comparing to the bulk material of that at 370 nm. The PL spectra show that ZnO QDs exhibit UV emission with a narrow wavelength from 375 nm to 381 nm, while the ZnO bulk materials have a PL emission peaked at 387 nm.[11] The blue shift of PL spectra is due to the so-called quantum size effect. When the density of ZnO is low, ZnO QDs are individually dispersed in the solution. It is supposed that with the increase of the density of ZnO QDs, some of them are coupled with two or more particles to form clusters, which decreases the quantum size effect and leads to red shift of the absorption and PL spectra. Their agglomeration mechanisms will be discussed in detail in next section.

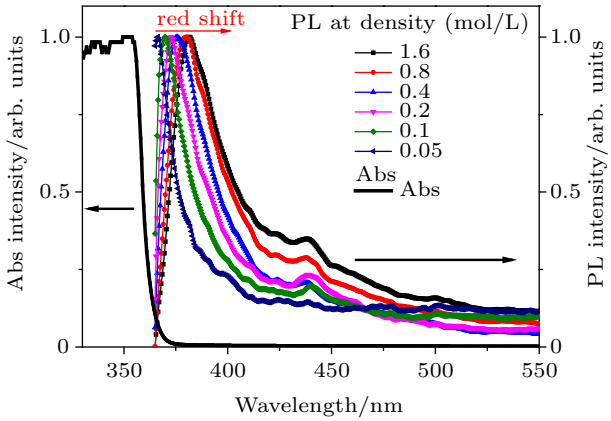


Fig. 3. (color online) Absorbance spectra with an absorption edge of 359 nm and photoluminescence spectra in ethanol peaked from 375 nm (3.31 eV) to 381 nm (3.25 eV) of ZnO QDs.

It is quite significant to achieve ZnO quantum dots from colloidal to solid state with high dispersion. The film of ZnO QDs is shown in Fig. 4 which is applied on film devices. The film requires uniform and high dispersion of QDs. Hence, it is pressing to unclear the agglomeration mechanism of quantum dots and to find pathways to avoid their agglomeration.

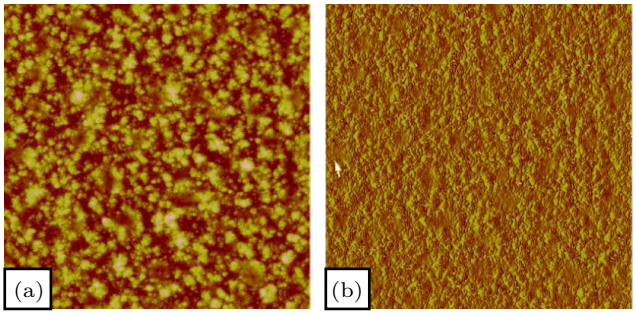


Fig. 4. (color online) AFM images of ZnO quantum dots on Si (001): (a) topography image and (b) phase image.

3.3. The agglomeration mechanisms of ZnO QDs

In order to make clear the agglomeration mechanisms of ZnO QDs, we carried out the ageing of ZnO QDs with time and temperature as shown in Fig. 5. The ZnO QDs congregate after ageing for 30 days, much more at 25 °C than at 0 °C. The PL spectra of aged ZnO QDs are shown in Fig. 6. Compared to Fig. 3, the PL emission at UV domain decreases dramatically. Meanwhile, the PL emission at 550 nm increases, which is due to the defect emission. Note that in the solution of ethanol, the dangling bonds increase sharply with time. The active dangling bonds easily react with molecules in the circumstance, forming impurities and other surface defects, which will eventually increase the defects emission and decrease the excitons

emission. The exciton emission, impurity, or surface states emission[12,13] are the main luminescence pathways of ZnO QDs, which are competing with each other. In order to increase the exciton emission, the others should be restrained and the agglomeration mechanisms of ZnO QDs need to be investigated.

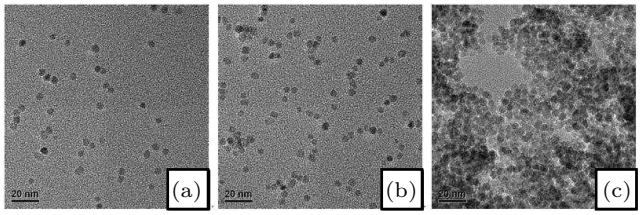


Fig. 5. TEM images of (a) freshly prepared, (b) ageing for 30 days at 0 °C and (c) ageing for 30 days at 25 °C.

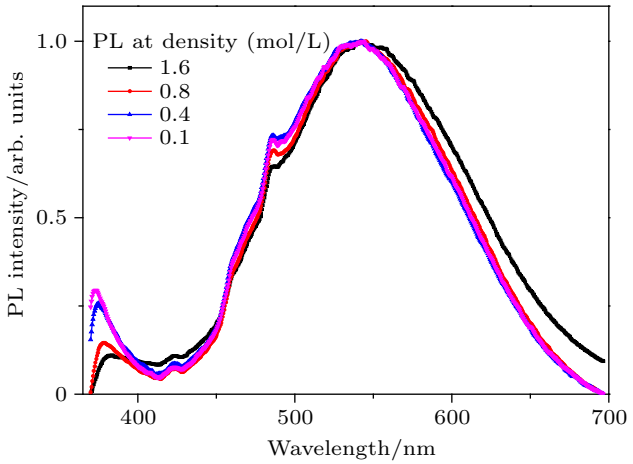


Fig. 6. (color online) PL spectrum of ZnO QDs after ageing for 30 days at 25 °C.

Interestingly, the agglomeration of QDs is accompanied by the emission spectra at 550 nm that are related to the defect emission. Hence, in order to unclear how the QDs agglomerate in the solvent and its relationship with the defect emission spectra, it is necessary to uncover what kind of chemical bonds or ions and possible hanging bonds at the surface of QDs.

The ions and hanging bonds generate during the formation of ZnO QDs in solvent. The reaction equations of ZnO QDs formation are given as follows:

$$\mathrm{Zn(CH_3CO_2)_2 + 2LiOH \rightarrow ZnO + H_2O + 2LiCH_3CO_2}. \quad (2)$$

In the reaction system, the ZnO QDs result from the dehydration reaction of $\mathrm{Zn(OH)_4^{2-}}$ unit, with possible chemical equations

$$\mathrm{Zn\,(CH_3COO)_2 \rightarrow Zn^{2+} + 2CH_3COO^-}, \quad (3)$$

$$\mathrm{LiOH \rightarrow Li^+ + OH^-}, \quad (4)$$

$$\mathrm{Zn^{2+} + 4OH^- = Zn\,(OH)_4^{2-}}, \quad (5)$$

$$\mathrm{Zn\,(OH)_4^{2-} + Zn\,(OH)_4^{2-} \rightarrow Zn_2O\,(OH)_6^{4-} + H_2O}, \quad (6)$$

$$\mathrm{Zn_xO_y\,(OH)_z^{(z+2y-2x)-}\,(nucleus) + Zn\,(OH)_4^{2-}}$$

$$\mathrm{= Zn_{x+1}O_{y+1}\,(OH)_{z+2}^{(z+2y-2x+2)-} + H_2O}. \quad (7)$$

During the preparation of QDs, $\mathrm{Zn\,(CH_3COO)_2}$ in ethanol generates ions like $\mathrm{Zn^{2+}}$ and $\mathrm{CH_3COO^-}$, LiOH generates ions like $\mathrm{Li^+}$ and $\mathrm{OH^-}$. When the $\mathrm{Zn\,(CH_3COO)_2}$ solution drops in the LiOH solution gradually, the ions $\mathrm{OH^-}$ and $\mathrm{Zn^{2+}}$ collide with each other, generating $\mathrm{Zn(OH)_4^{2-}}$ unit. Under diffusion of ions and collision between molecules and ions, $\mathrm{Zn(OH)_4^{2-}}$ unit reunions through dehydration reactions, forming ZnO QDs. Some of these ions still cling to the surface of the QDs even after purified. Meanwhile, the prepared QDs have significantly high surface energy and dangling bonds.

The freshly prepared ZnO QDs model is shown in Fig. 7(a) with high dispersion, and the surface of QDs is surrounded by the solution. However, because of the small size (approximately 4.8 nm), high specific surface area, and much of surface dangling bonds at the surface, active surface energy, ZnO QDs are prone to agglomerate. The particles move irregularly in the solution (see Fig. 7(b)) and grow larger and larger (see Figs. 7(c) and 7(d)) due to the effect of electrostatic attraction, Van der Waals' force, and solvent thermal motion, which is similar to the Brownian motion processes. The ZnO QDs collide with each other to form a bigger cluster, then the cluster grows bigger and bigger. Meanwhile, the ZnO QDs can be also dispersed which is called soft agglomeration. After ageing for a long time, the clusters become hard agglomeration with strong bonds, which is difficult to disperse.[14] In summary, the formation of clusters and the increase of defects decrease the quantum size effect and lead to the red shift of the emission spectra.

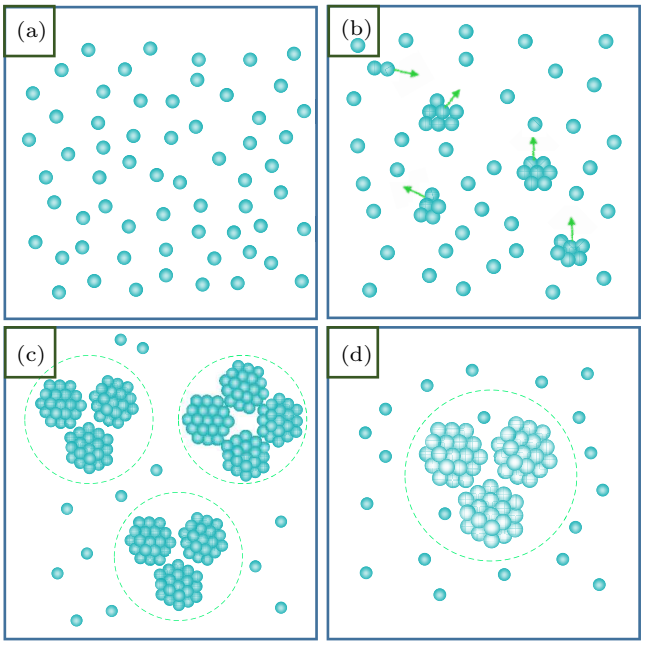


Fig. 7. (color online) The agglomeration mechanisms of ZnO quantum dots, from individually dispersed to coupled with number of QDs in the cluster. (a) ZnO QDs are highly dispersed; (b) the particles move irregularly in the solution and form clusters; (c) the clusters grow larger and larger; (d) hard agglomeration with strong bonds is formed.

The key factors that lead to agglomeration are the density of ZnO QDs, ageing temperature, and ageing time. Hence, for each factor, the solution can be carried out to solve the agglomeration problems. One possible pathway is to embed them in polymer matrices or colloid to preserve their dispersed state,[15,16] which nevertheless, may decrease the semiconductor electrical properties. Another possible way to solve the problem is to build core-shell structure, by using surfactant, by doping element or ions.[17–19] However, the ZnO QDs and other QDs materials are potential semiconductor materials in electronic devices, such as lasers, OLEDs, and photovoltaic devices, the usual shell materials or doping materials may reduce surface defects and meanwhile bring adverse effect on the electronic and luminescent properties of QDs.[20–24] Another possible way is to keep them at relatively low temperature in closed cavity to avoid contact with the atmosphere, such as in glass capsules, for long service time in device. Further methods of solving the problem of stability of QDs need to be developed to utilize the QDs with high efficient quantum size effect.

4. Conclusion and perspectives

In summary, uniform small size of ZnO QDs were prepared and characterized. The ZnO QDs are highly crystallized in wurtzite structure. The absorption edge and photoluminescence peak blue-shift due to the quantum size effect. However, the photoluminescence peak red-shifts with the increase in ZnO density because of the agglomeration of them. The agglomeration mechanisms and their relationship with the emission spectra were uncovered for the first time. ZnO QDs collide to form bigger clusters with much more impurities and surface defects, which leads to the defect emission and restrains the exciton emission. It provides a clue to realize the stable quantum effect of ZnO QDs for electronic applications.

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