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Stable Aqueous Dispersion of ZnO Quantum Dots with Strong Blue Emission via Simple Solution Route

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Abstract: The aqueous dispersion of ZnO quantum dots (QDs) with strong blue emission (quantum yield of 76%) was synthesized through a simple solution route. The water stability of such QDs is provided by the hydroxyl groups on their surface, and the strong blue emission is suggested to arise from the formation of surface ZnO/oleic acid complexes. Under irradiation, these complexes are thought to absorb the excitation light with 3.54 eV and then generate the blue emission with 2.82 eV.

Introduction

Synthesis of quantum dots (QDs) with narrow size distribution and high luminescent efficiency has attracted intensive interest in the past decade due to their wide applications in biological fluorescence labeling.¹ ZnO is an environmentally friendly oxide semiconductor and inexpensive luminescent material compared with traditionally used QDs of CdSe or CdTe, which makes it more attractive for practical applications.² To date, the most successful approach to obtain quantum-sized ZnO in dispersions has been the sol–gel route.³ However, colloidal ZnO nanocrystals tend to aggregate or undergo Ostwald ripening owing to their high surface energy.⁴ As a result, such nanocrystals are unstable in aqueous dispersions during storage.⁵

In general, two emission peaks appear in the ultraviolet (UV) and visible region in the photoluminescence (PL) spectra of ZnO QDs. In the visible range, the blue emission of ZnO QDs is normally not as bright as the green-yellow one.⁶ Although the origin of the blue emission was proposed to be special surface states or a trapping effect in QDs, any experimental evidence for a reasonable luminescence mechanism is still unavailable.⁷

Blue emission is in demand for biological fluorescence labeling and full-color display.⁸ To prepare stable ZnO QDs with strong blue emission, various techniques have been employed, including coating ZnO nanocrystals with organic molecules^{7b,9} or inorganic SiO₂ shells¹⁰ and in situ initiating polymerization on nanoparticle surfaces.¹¹ These surface modification methods are effective in obtaining stable ZnO colloids, which are usually well dispersed in organic solvent. However, the majority of bioanalyses require water-stable materials, and in this regard, the synthesis of water-stable ZnO QDs with blue emission is still far from successful.^{7a} Therefore, development of methods producing stable and water-dispersed ZnO nanoparticles with strong blue emission and an understanding of PL mechanisms in such systems are highly anticipated.

Since surface modifications have a significant impact on various properties of ZnO QDs,¹² it would be attractive to realize water stability and blue emission simultaneously by designing and controlling the surface chemistry. Herein, we report the synthesis of water-stable ZnO QDs with strong blue emission using a simple solution route, where Zn(NO₃)₂, diethanolamine (DEA), and oleic acid (OA) are carefully selected as starting materials. DEA can provide OH[−] ions for the synthesis of ZnO QDs and their stability in water, while OA seems to be crucial for the surface states giving the blue luminescence. Compared with previous reports, this one-pot process is simple and easy to be industrialized. The as-prepared product gives a strong blue emission with the quantum yield as high as 76%. Based on the

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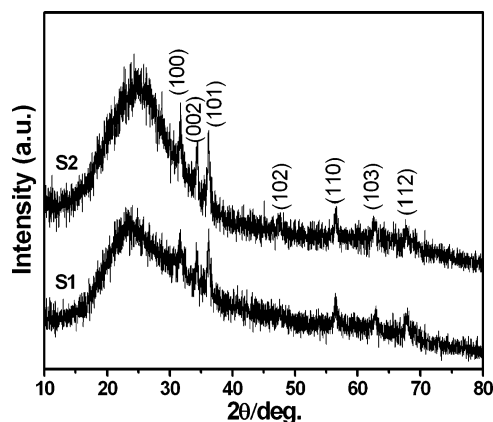


Figure 1. XRD patterns of S1 (with OA) and S2 (without OA). Positions of ZnO peaks are labeled.

experimental results, the origin of the blue emission appears to be the interface states related to ZnO/OA complexes.

Experimental Section

Sample Preparation. To prepare sample S1, 26.3 mg of DEA were dissolved into 50 mL of distilled water to obtain a 5.0 mM DEA solution, and 37.2 mg of zinc nitrate hexahydrate were dissolved into 50 mL of distilled water to form a 2.5 mM zinc nitrate solution; the above two solutions and 0.35 mmol of OA were added into a reactor together. After the mixture stirred at room temperature for 30 min and the temperature was increased to 80 °C with continuous stirring for another 2.0 h, stable ZnO nanoparticles are formed in the solution. The as-prepared dispersion was filtered, and then the dispersion was centrifuged and as-obtained product was redispersed subsequently with 1-butanol, 1-propanol, and ethanol to remove any unreacted molecules. Finally, the QDs were obtained by centrifugation and then dispersed in water for further characterization. Sample S2 was prepared under the same conditions but without OA added. Samples S3 and S4 were prepared using the same recipe and process as those for S1 except for substituting DEA with ammonia or using 4.0 mM aqueous zinc nitrate, respectively.

Characterization. The X-ray diffractometry (XRD) for the crystal structure of the freeze-dried products was carried out in a Rigaku D/max 2500v/pc diffractometer. The morphology of samples was observed using a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. Transmission electron microscopy (TEM) samples were prepared by dropping dilute products onto carbon-coated copper grids. Fourier transform infrared (FTIR) spectra of purified and dried nanoparticles were recorded using an attenuated total reflection FTIR Nicolet 470 spectrometer. UV–vis absorption spectra were recorded on a Philips 3000 spectrophotometer. PL and photoluminescence excitation (PLE) analyses with a Hitachi F-4500 fluorescence spectrometer were performed on aqueous solutions directly at room temperature using 350 and 432 nm as the excitation and detection wavelengths, respectively. The photostability property was investigated by measuring the intensity change of the 440 nm PL peak under the irradiation of 350 nm UV light with a power density of 130 $\mu\text{W}/\text{cm}^2$. To evaluate the quantum yield (QY) of the ZnO nanoparticles, quinine sulfate in 0.5 M sulfuric acid was used as a reference.¹³

Results and Discussion

Typical XRD patterns of samples S1 and S2 are shown in Figure 1. The patterns fit well with zinc oxide with wurtzite structure (JCPDS Card No. 89-1397), which indicates both

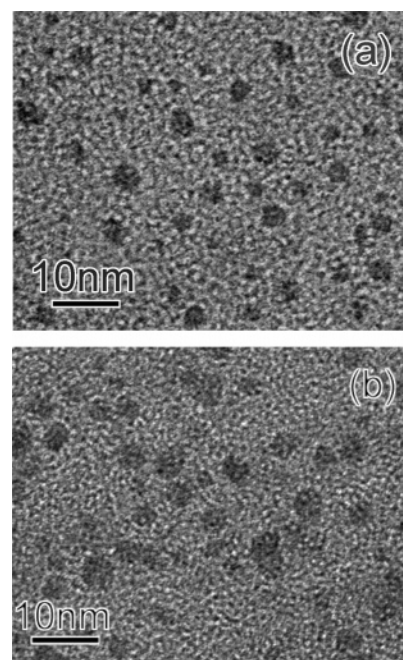


Figure 2. HRTEM images of (a) S1 (with OA) and (b) S2 (without OA).

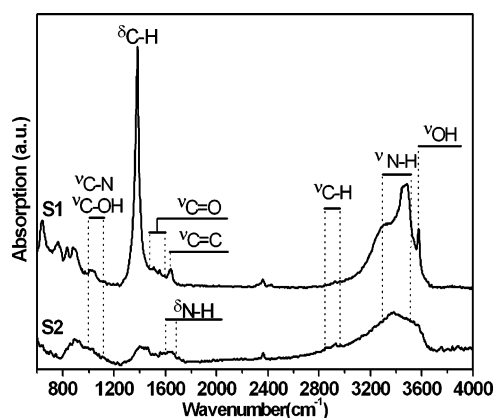


Figure 3. FTIR spectra of purified and dried ZnO QDs from S1 (with OA) and S2 (without OA).

samples contain ZnO crystals. The broad diffraction peak located at $\sim 25^\circ$ arises from the glass substrate.

Figure 2 presents high-resolution TEM (HRTEM) images of S1 and S2. The ZnO QDs in both samples are seen to be uniform and disperse. The size of nanocrystals in S1 is about 3.8 ± 0.4 nm, which is smaller than that in S2 (5.0 ± 0.5 nm).

As seen from the FTIR spectrum of purified and dried powder of S1 in Figure 3 (top spectrum), the peak at 1640 cm^{-1} is attributed to C=C groups in OA, and two peaks in the range of $1400\text{--}1600\text{ cm}^{-1}$ are attributed to the stretching vibrations of C=O groups in surface ZnO/OA complexes similar to those previously reported by others.¹⁴ The stretching vibrations of C=O groups ($1700\text{--}1725\text{ cm}^{-1}$) from free OA are not detected, thus confirming the OA is chemically bonded to the particles in S1. Moreover, the peak at $\sim 3300\text{--}3600\text{ cm}^{-1}$, assigned to the $\nu(\text{N-H})$ mode, implies there are also DEA molecules on the surface of the nanoparticles. This is also consistent with

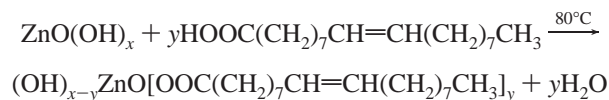
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the peak at 3300–3600 cm^{-1} attributed to the $\nu(\text{OH})$ vibration mode, which could also be from surface adsorbed DEA.

The vibration of surface-free ZnO was reported to be only located at 450 cm^{-1} .¹⁵ However, the FTIR spectrum of purified and dried powder of S2 (Figure 3, bottom) shows peaks at 1000–1100 cm^{-1} , 1600–1650 cm^{-1} , 2850–3000 cm^{-1} , and 3300–3600 cm^{-1} , which are assigned to $\nu(\text{C}-\text{N})$ and $\nu(\text{C}-\text{OH})$, $\delta(\text{N}-\text{H})$, $\nu(\text{C}-\text{H})$, $\nu(\text{N}-\text{H})$, and $\nu(\text{OH})$, respectively. Hence, the ZnO nanoparticles in S2 appear to have surface-adsorbed molecules of DEA and hydroxyl groups, the latter being responsible for good water stability.

The FTIR results in Figure 3 illuminate the evolution of surface-bonded organic molecules on ZnO QDs. For S2 without OA addition, ZnO QDs could be synthesized through the hydrolysis of $\text{DEA}-\text{Zn}^{2+}$ complexes starting at a lower temperature of $\sim 60^\circ\text{C}$ (see Supporting Information, part 1), and DEA molecules and hydroxyl groups were found on the surface of the particles, in agreement with previous work.¹⁶ As for S1 with OA, the ZnO particles are also thought to form first at lower temperature. Then, as the temperature is elevated to 80°C , OA is expected to react with hydroxyl groups attaching on the surface of ZnO QDs:



As a result, covalently bonded OA molecules appear to form on the surface of ZnO QDs in S1. Since OA is known for its surfactant-like behavior, the appearance of such OA molecules on the ZnO QDs is expected to provide their excellent stability in aqueous dispersion. On the other hand, as DEA molecules were also found on the particle surface, their OH groups should contribute to the observed water stability of the nanocrystals too.

Figure 4a shows PL and PLE spectra. A strong blue emission around 440 nm (2.82 eV) is evident in the PL spectrum of sample S1, and the PLE spectrum shows the optimal excitation wavelength for the blue emission is 350 nm (3.54 eV) (Figure 4a, top). Correspondingly, the direct photograph of this sample (Figure 4b, S1) under UV irradiation demonstrates a strong blue emission. A high QY of about 76% was evaluated for S1 (see Supporting Information, part 2), which implies some structural peculiarities of the sample synthesized with OA. In comparison, S2 does not show any luminescence both in the PL spectrum and in Figure 4b.

Photostability is one of the major problems of traditional dyes for bioimaging.¹⁷ Comparatively, the light emission from the ZnO–oleic acid system is generally stable. As shown in Figure 4c, the intensity of the 440 nm PL peak decreased by 9.4% during the first 6 h and then remained almost unchanged.

To clarify the origin of the intense blue emission from S1, first solutions of DEA and OA in water, as well as mixtures thereof, were tested. The measurements indicate no blue emission from any of such solutions.

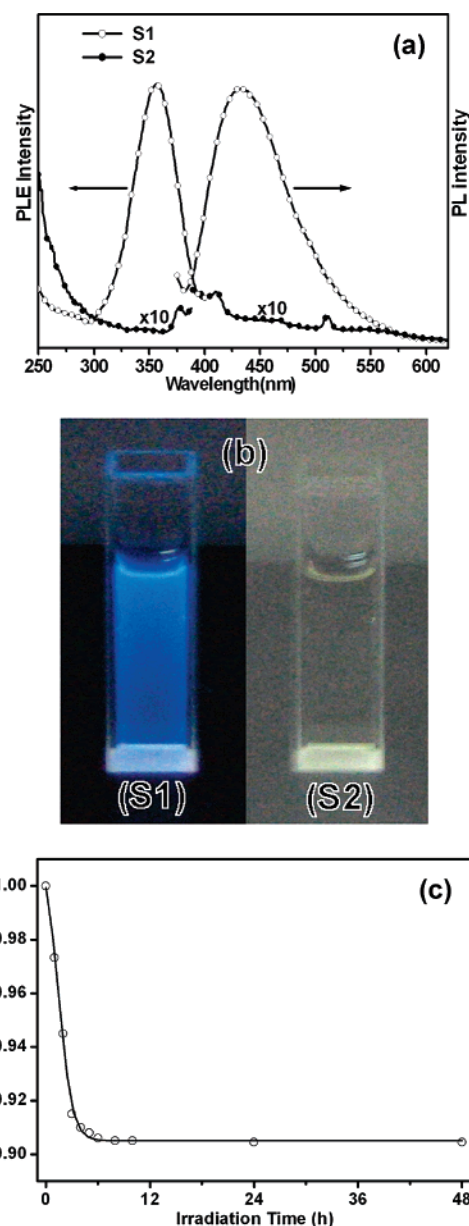


Figure 4. (a) PL and PLE spectra of S1 (with OA) and S2 (without OA). Samples were excited by 350 nm light, and their PLE spectra were recorded with a detection wavelength of 432 nm. (b) Direct photographs of S1 and S2 under irradiation by a 350 nm UV lamp. (c) Relative PL intensity of 440 nm PL peak from S1 versus irradiation time under 350 nm light irradiation.

The possibility of the blue emission originating from the ZnO QDs themselves was also considered. The optical absorption spectra of S1 and S2 are presented in Figure 5a. ZnO is a direct-band gap semiconductor, and therefore its absorption coefficient is related to the excitation energy ($E_{\text{exc}} = h\nu$) by $(\alpha h\nu)^2 = \text{const} \cdot (h\nu - E_g)$, where E_g is the band gap energy.¹⁸ To obtain the absorption onset, $(\alpha h\nu)^2$ was plotted versus energy $h\nu$ (Figure 5b). Extrapolation of the linear part until its intersection with the $h\nu$ axis gives the values of E_g . From Figure 5b, E_g values are 3.94 eV for S1 and 3.67 eV for S2, both of them showing a blue shift compared to the band gap for bulk ZnO (3.37 eV).

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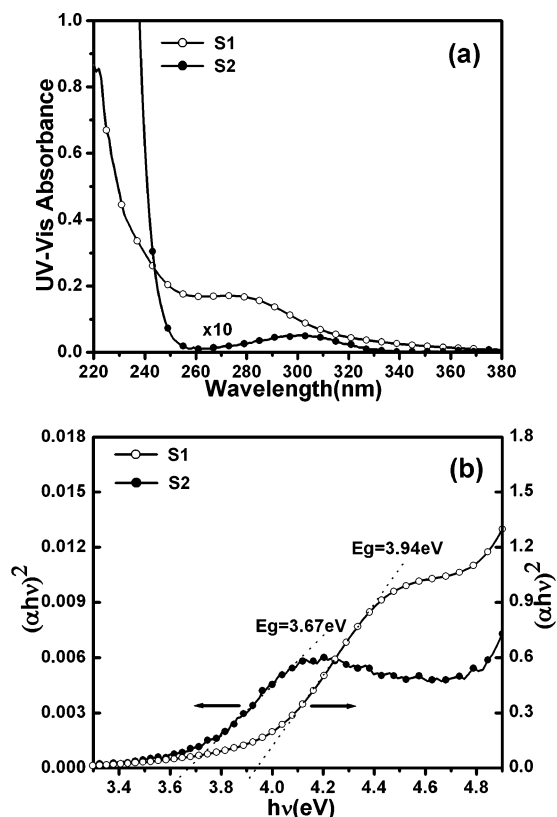


Figure 5. (a) UV-vis absorption spectra of S1 (with OA) and S2 (without OA); the absorption intensity of S2 is multiplied 10 times. (b) $(\alpha h\nu)^2$ versus $h\nu$ plot for determining absorption onset of S1 and S2.

Theoretically, a blue shift of the absorption edge of QDs arising from a quantum confinement effect can be described as follows:¹⁹

$$E_{(\text{gap,dot})} = E_{(\text{gap,bulk})} + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 0.248E_{\text{Ryd}}^*$$

where $E_{(\text{gap,dot})}$ and $E_{(\text{gap,bulk})}$ are band gaps of QDs and bulk ZnO, respectively. E_{Ryd}^* , R , and h are the bulk exciton binding energy (60 meV), particles' radius, and Plank's constant, respectively; $m_e^* = 0.24m_0$ and $m_h^* = 1.8m_h$ are the effective masses of electron and hole, respectively. According to statistical results from TEM images, the average particle diameters in S1 and S2 are 3.8 and 5.0 nm, respectively. By adopting the above equation, the theoretical band gaps for S1 and S2 are determined as 3.92 and 3.68 eV, which are consistent with the experimental values from Figure 5b.

There is a large energy difference of about 1.12 eV between the absorption onset at 3.94 eV and the emission line at 2.82 eV (440 nm) for sample S1 in Figure 4a. It is larger than the highest red shift, 0.39 eV, caused by electron-phonon coupling, lattice distortions, and localization of charge carriers in ZnO QDs.²⁰ On the other hand, based on the PLE spectrum in Figure 4a, the optimal excitation energy for the blue emission from S1 is 3.54 eV (350 nm), which is lower than the band gap of ZnO QDs (3.94 eV). Therefore, the strong blue emission is clearly not from ZnO QDs.

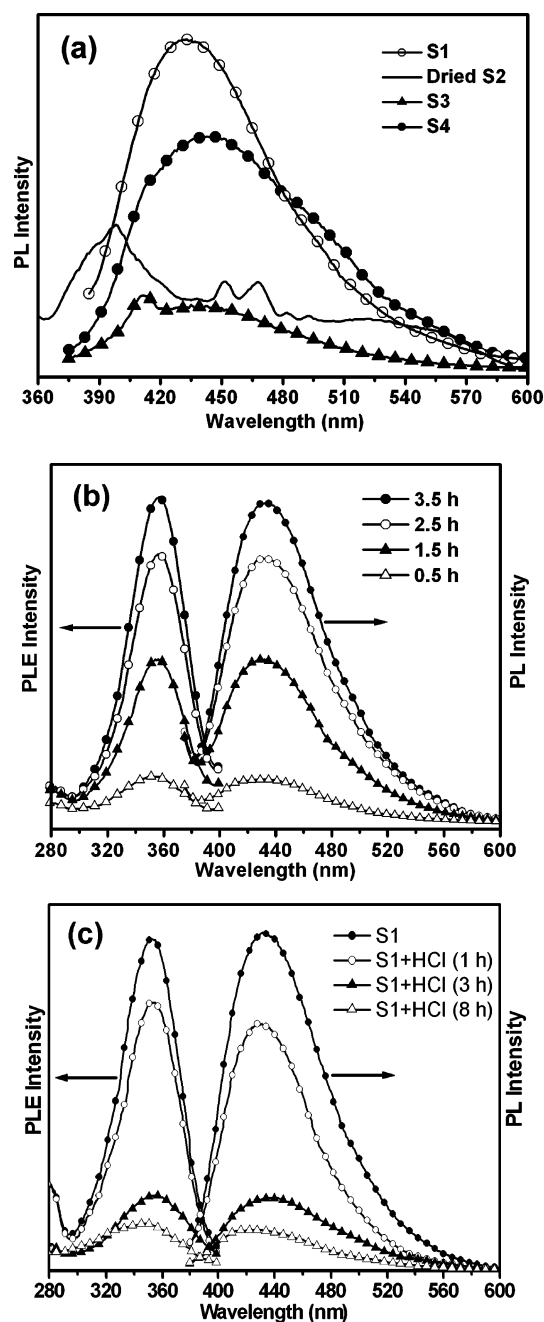


Figure 6. (a) PL spectra of samples S1, S2 (dried powder), S3 (PL intensity of the latter being multiplied 10 times), and S4. (b) Time evolution of PL and PLE spectra of heated mixture of S2 and OA from 0.5 to 3.5 h. (c) Time evolution of PL and PLE spectra of heated mixture of S1 and HCl over time range from 1 to 8 h.

Previous works suggested the blue emission of ZnO QDs originated from special interface species or trapping effects at the particles surface.^{7,9,11} In our case, surface-bonded OA molecules are proven to exist on the surface of the nanoparticles, and thus they could produce interface states responsible for the blue emission observed. To verify the relevance of this assumption, several control experiments were conducted.

In the first experiment, PL test was performed on a dry powder of S2 synthesized without OA. As seen in Figure 6a (solid line), such nanoparticles only emitted strong UV light at 392 nm and weak blue light at 450 and 479 nm. This clearly proves that OA molecules are necessary for the strong blue emission of the final product.

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In the second test, sample S3 was prepared using the same recipe and process as those for S1 except for substituting DEA with ammonia. As seen in Figure 6a (triangles), S3 only shows a weak visible PL emission in a wide wavelength range. This experiment verifies DEA molecules used in the synthesis also play a special role and thus cannot be replaced by, e.g., ammonia. Although this role is not yet clear in detail, it is believed that DEA provides surface hydroxyl groups which then react with carboxyl groups from OA producing the carboxylate groups. The latter, being a constituent part of surface ZnO/OA complexes, are likely to be involved in the blue emission.

In the third experiment, sample S4 was prepared using the same recipe and process as those for S1 except for increasing the concentration of $\text{Zn}(\text{NO}_3)_2$ to 4.0 mM. Based on the HRTEM image (see Supporting Information, part 3), the average particle size of S4, 4.2 nm, is somewhat bigger than that of S1 (3.8 nm). The amount of $\text{Zn}(\text{NO}_3)_2$ and that of DEA in the recipe of S1 accord exactly with the stoichiometric ratio for producing ZnO, and the only increase in the concentration of $\text{Zn}(\text{NO}_3)_2$ hardly changes the total amount of ZnO in S4; therefore, as the particle size increases, the number, as well as the total surface area, of ZnO particles in S4 should be reduced. Correspondingly, the spectra in Figure 6a illustrate that the PL intensity of S4 is lower than that of S1, which reveals a correlation between the PL intensity and the surface area of ZnO particles and suggests that the blue emission is a surface-related behavior. On the other hand, as the particle size increases from 3.8 to 4.2 nm, the reduction of the total surface area was estimated to be 9.5%, while the PL intensity decreases by 28.8%. This indicates a nonlinear relationship between the PL intensity and the surface area.

In the fourth experiment, a mixture of as-prepared S2 (20 mL) and 0.35 mmol of OA was heated at 80 °C from 0.5 to 3.5 h. As seen in Figure 6b, PL and PLE measurements for aliquot samples taken after certain periods of time show the emission and excitation increase with reaction time. These observations allow us to conclude that surface hydroxyl groups on the S2 nanoparticles react with OA producing QDs with surface chemistry close to that of S1. The excitation and emission intensity in Figure 6b seem to be related to the number of surface-bonded OA molecules, which is proportional to the reaction time.

In the final experiment, several drops of diluted HCl were added into S1, and the solution was heated at 80 °C for several hours. ZnO particle cores could be dissolved by HCl, thus destroying the interface states, and as a result, the intensity of the PLE and PL peaks is observed to decrease gradually with the aging time (see Figure 6c). This experiment verifies that the interface states, as well as the PL and PLE peaks, correlate with the ZnO particles too.

All these experiments lend support to the assumption that the blue emission arises from nothing but the complex of surface-bonded OA and ZnO nanoparticles. This conclusion is consistent with the assumptions on the blue emission resulting from interface-related phenomena on the surface of ZnO nanoparticles^{7a,9,11} rather than the hole trapping effects.^{7b} However, our work points out that it is the interface states related

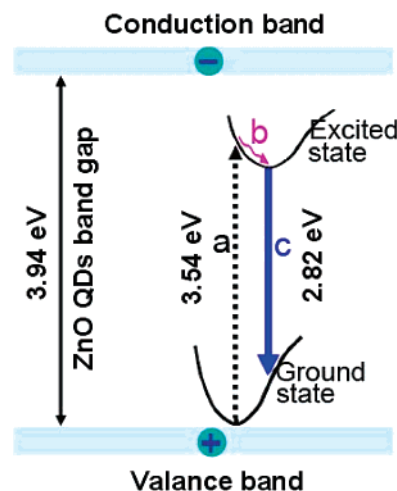


Figure 7. Scheme of the blue luminescence process in ZnO QDs with ZnO/OA-related interface states.

to the surface-bonded molecules of OA that are most likely to be the origin of the blue emission observed in this study.

Based on the above, we propose a mechanism of the strong blue emission observed as follows. As shown in Figure 7, the ground state and the first excited state of the interface states are located in the band gap of ZnO QDs. Under an appropriate excitation of 3.54 eV, the absorption of such interface states reaches its maximum by exciting the electrons from the ground state to the first excited state (step a). After this, the interface states can rapidly dissipate their excess vibrational energy through vibration relaxation and reach the lowest vibrational level of the first excited state (step b). The further transition from the excited state to the vibrational level of the ground state gives rise to the blue emission with an energy of 2.82 eV (step c).

Conclusions

In conclusion, a stable aqueous dispersion of ZnO QDs with strong blue emission has been synthesized via a simple solution route. The water stability of such ZnO QDs appears to arise from the adsorption of OA and the enhancement in hydroxyl groups on their surface, and the strong blue emission is suggested to be a result of the formation of surface-bonded molecules of OA. Such ZnO water-disperse nanoparticles with stable and intense blue fluorescence are expected to be of use for further processing, assembly, or practical applications.

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Supporting Information Available: An HRTEM image of ZnO QDs formed at low temperature and description of the procedure to evaluate the fluorescence quantum yield (QY) of S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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