

Fluorescence Property of ZnO Nanoparticles and the Interaction with Bromothymol Blue

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Abstract We synthesized ZnO quantum dots (QDs) simply in alcoholic solution, and investigated the interaction between ZnO QDs and bromothymol blue. The structural, morphological, size and spectral properties of ZnO QDs were studied. It was found that ZnO QDs were spherical nanoparticles in the crystal structure, and the average diameter of ZnO QDs was about 4.8 nm. The excitation and emission peaks were located at 346 nm and 520 nm, respectively, which were obtained on a common fluorophotometer. The quantum yield of ZnO QDs was obtained by using quinine sulfate as a reference reagent. In addition, the fluorescence of ZnO QDs can be quenched by bromothymol blue, and the quenching mechanism was proposed in a dynamic quenching mode.

Keywords ZnO QDs · Bromothymol blue · Fluorescence quenching

Introduction

Recently, extensive studies have been carried out on the fluorescence of nanoparticles, because of unique optical properties [1]. Owing to the effect of quantum confinement, colloidal semiconductor nanocrystals also called quantum dots (QDs), show exceptional physical and chemical properties such as sharp and symmetrical emission spectra, high quantum yield (QY), good photo- and chemical stability, and size-dependent emission-wavelength tenabili-

ty [2–4]. ZnO is an interesting direct-band-gap II–VI semiconductor with wurtzite-type structure, which consists of the hexagonal lattice with a c/a ratio of 1.602. Its bandgap is 3.37 eV and excitonic binding energy is 60 meV at room temperature. Due to above optical properties, it is useful as a candidate material for various technological applications such as short-wavelength light emitters [5], field emitters [6], luminescence devices [7], UV lasers [8], and solar cells [9, 10].

There are powerful fluorescence methods based on the measurement and interpretation of the quenching of fluorophores under controlled experimental conditions. In these studies special molecules, so-called quenchers—which can quench the fluorescence emission—are applied, and the procedure was named fluorescence quenching. Fluorescence quenching has been successfully exploited in the pursuit of understanding complex macromolecular systems both chemistry and biology in nature.

It was reported that ZnO nanoparticles could quench the fluorescence of tryptophan, in this case the static mode of fluorescence quenching occurred [11]. However, there has been no work so far to investigate the quenching effect on the fluorescence of nanostructural ZnO. In this work, the structure, morphology, size, and fluorescence properties of ZnO QDs have been studied, and the QY was obtained by comparison with quinine sulfate—a common reference material. It was found that the fluorescence of ZnO QDs was quenched in the presence of bromothymol blue, and the quenching mechanism was owing to the dynamic quenching mode which was also called collisional quenching. The quenching constant was calculated. It will be useful for studying the interaction mechanism between ZnO QDs and other compounds such as drugs, dyes, and biomacromolecules.

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Experimental Section

Sample Preparation

The conventional ZnO nanoparticles without modification are unstable in water because water will exchange the organic protecting groups on the ZnO surface, destroy the luminescent centers, and render ZnO nanoparticles aggregates [12]. In this case, anhydrous ethanol was used as the solvent throughout the whole experiment including washing and sampling except special explanation. ZnO nanocolloids suspension was prepared by modifying a reference method [13]. Simply, 5 ml of 0.02 mol l^{-1} NaOH from stock solutions was piped to a flask and diluted with 30 ml anhydrous ethanol. 0.625 ml of 0.04 mol l^{-1} $\text{Zn}(\text{CH}_3\text{COO})_2$ ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ from Fluka) in ethanol was then added within 5 min under vigorous stirring. After 40 min, 13.75 ml anhydrous ethanol and 0.625 ml of the $\text{Zn}(\text{CH}_3\text{COO})_2$ solution was introduced, in which Zn^{2+} and OH^- was stoichiometric reaction. As a result, the transparent 1 mmol l^{-1} ZnO QDs were obtained after continuous stirring for 24 h.

Characterization

The X-ray diffractometry (XRD) for the crystal structure of ZnO nanoparticles was carried out in a XD-3 powder diffractometer (Purkinje General Instrument Co. Ltd., Beijing, China). The morphology of samples was observed using a Philips Tecnai G2 microscope with a field-emission gun operating at 200 kV. High-resolution Transmission electron microscopy (HRTEM) samples were prepared by dropping dilute products onto carbon-coated copper grids. UV–vis absorption spectra were recorded on a Lambda-40 UV–vis spectrophotometer (Perkin Elmer, USA). Fluorescence spectra and excitation analyses were performed on a LS-55 fluorescence spectrometer equipped with a computer collecting data, using 340 nm and 520 nm as the excitation and detection wavelengths, respectively. To evaluate the QY of the ZnO nanoparticles, quinine sulfate in 0.5 mol l^{-1} sulfuric acid was used as a reference [14].

Fluorescence Measurement

Fluorescence signal was detected in a right angle viewing mode for the incident light and that of emission. Excitation and emission slits were set both at 5.0 nm band-pass. In the process, appropriate volume of ZnO QDs and a series of bromothymol blue standard solutions were added to the 10.0 ml comparison color tube, diluted by ethanol and homogenized for determination. The detection spectra were obtained in the range of 420–650 nm ($\lambda_{\text{max}}=520 \text{ nm}$) with the excitation wavelength at 340 nm. The whole process was carried out at the room temperature ($20 \text{ }^\circ\text{C}$), except for the special illustration.

Results and Discussion

Structural Characterization

Figure 1 shows XRD fingerprints of ZnO powder samples which were concentrated and dried from ZnO nanocolloids ethanol solution. It is indicated that the XRD patterns match with the as synthesized ZnO nanocrystals reported in the literature [15]. The spacing values and relative intensities of the peaks coincide with the JCPDS data, so the observed patterns can be unambiguously attributed to the presence of hexagonal wurtzite crystallites. By application of the Scherrer-Warren formula [16], the average crystallite size was calculated to be about 4.8 nm.

Figure 2 describes HRTEM image from above investigated samples, from which it can be seen that the ZnO nanoparticle is in a spherical shape, crystalline and non-agglomerated. The crystal lattice of ZnO QD is very clear as shown in the inset of Fig. 2. The nanoparticle size distribution has been determined to be relatively narrow with diameters of $4.8 \pm 0.3 \text{ nm}$, which is in a good agreement with the XRD data.

Fluorescence Properties

The UV–vis and fluorescence spectra of ZnO QDs are illustrated in Fig. 3. The optical absorption consists of a partially resolved band with a sharp onset corresponding to the excitonic transition of ZnO. The observed optical band gap of 346 nm can be related to the dimension of the nanoparticles, as the above XRD and TEM data show that the calculated ZnO particle size is 4.8 nm. The fluorescence spectrum of the ZnO QDs on excitation at 340 nm exhibits an intense broad emission band in the visible centered at

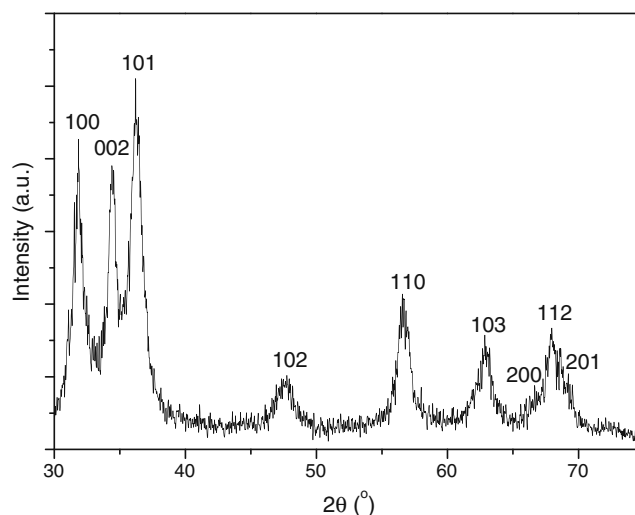


Fig. 1 XRD patterns of ZnO nanocolloids prepared freshly. Positions of ZnO peaks are labeled

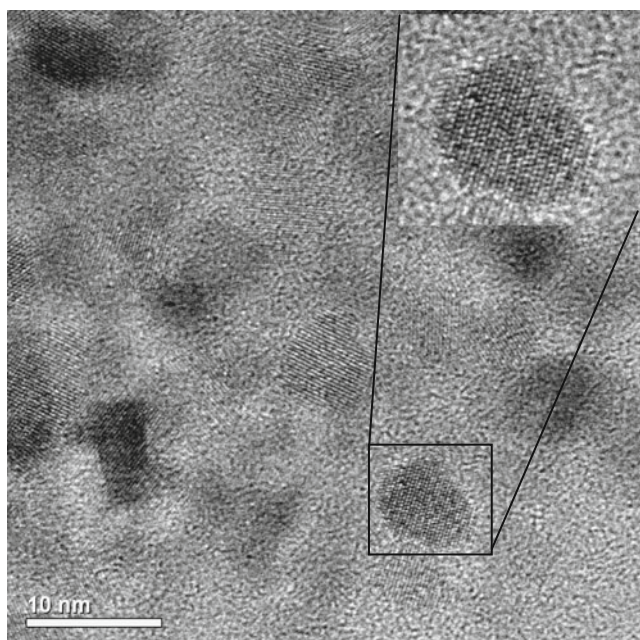


Fig. 2 HRTEM image of ZnO nanocolloids prepared freshly. An enlarged particle is seen in the inset

520 nm. For the mechanism of the green emissions, it is commonly referred to as a deep-level or trap-state emission and a number of different hypotheses have been proposed, such as transition between singly ionized oxygen vacancies and photoexcited holes [17], transition between electrons close to the conductive band and deeply trapped holes at $V_{O^{++}}$ [18], surface defects [19], etc. The excitation spectrum obtained by monitoring the emission at 520 nm is similar to the absorption spectrum.

The QY, Φ , of ZnO QDs sample was calculated by comparing the integrated fluorescence intensities (excited at

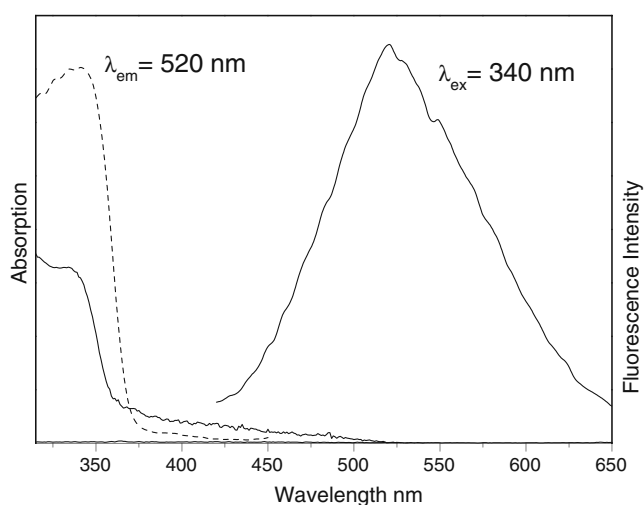


Fig. 3 Absorption and fluorescence spectra of ZnO nanocolloids. The excitation spectrum (dashed line) obtained by monitoring the emission at 520 nm

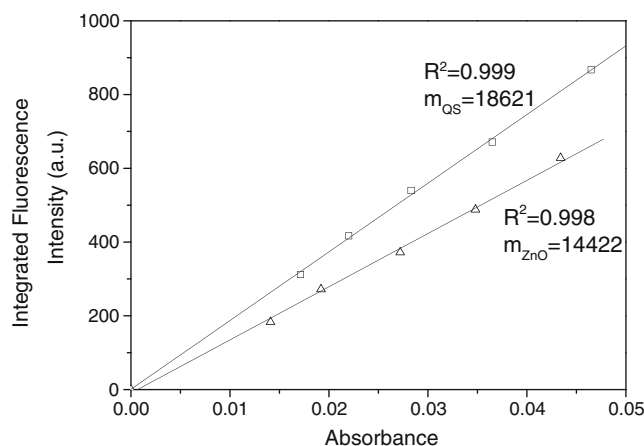


Fig. 4 Integrated fluorescence and absorbance of ZnO nanocolloids and Quinine Sulfate. \square Quinine Sulfate (QS); Δ ZnO nanocolloids

340 nm) and the absorbency values (at 340 nm) of ZnO nanocolloids with the reference quinine sulfate as illustrated in Fig. 4. Five concentrations of each compound were made, all of which had absorbance less than 0.05 at 340 nm. Quinine sulfate (literature $\Phi=0.55$) was dissolved in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ (refractive index, η , of 1.33). The ZnO QDs sample was dissolved in anhydrous alcohol ($\eta=1.36$). The QY was calculated using the below equation:

$$\begin{aligned} \Phi_{\text{ZnO}} &= \Phi_{\text{ST}}(m_{\text{ZnO}}/m_{\text{ST}})(\eta^2_{\text{ZnO}}/\eta^2_{\text{ST}}) \\ &= 0.55 \times (14422/18621)(1.36^2/1.33^2) = 0.45 \end{aligned}$$

Where Φ is the quantum yield, m is the slope (the gradient from the plot of integrated fluorescence intensity vs absorbance, i.e. Fig. 4), η is the refractive index of the solvent, and ST represents the standard, i.e. quinine sulfate.

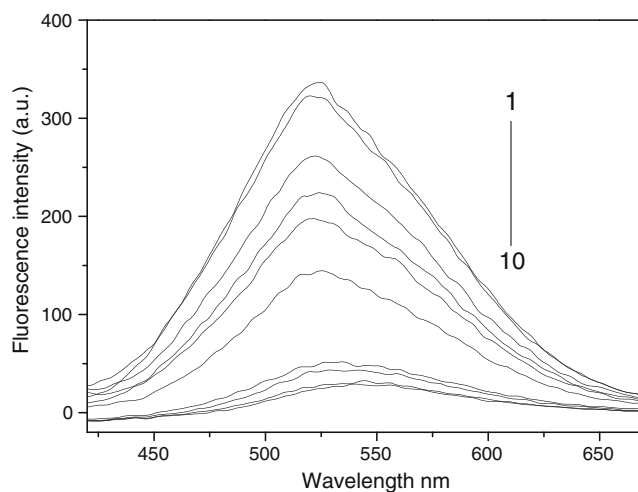


Fig. 5 Fluorescence spectra of ZnO nanocolloids with increasing concentration of bromothymol blue: 1 $0 \mu\text{mol l}^{-1}$, 2 $0.1 \mu\text{mol l}^{-1}$, 3 $0.5 \mu\text{mol l}^{-1}$, 4 $1.0 \mu\text{mol l}^{-1}$, 5 $3 \mu\text{mol l}^{-1}$, 6 $5 \mu\text{mol l}^{-1}$, 7 $10 \mu\text{mol l}^{-1}$, 8 $30 \mu\text{mol l}^{-1}$, 9 $50 \mu\text{mol l}^{-1}$, 10 $100 \mu\text{mol l}^{-1}$

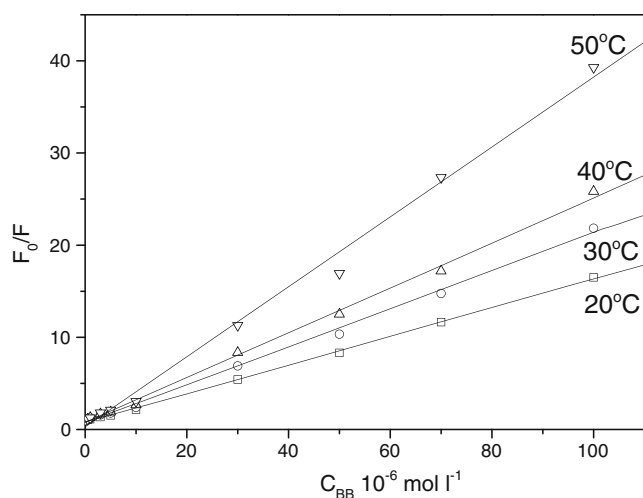


Fig. 6 Plots of F_0/F vs bromothymol blue concentration (CBB) under different temperatures. ZnO nanocolloids $30 \mu\text{mol l}^{-1}$

Quenching Effect of Bromothymol Blue on ZnO QDs Fluorescence

Fluorescence quenching is an important technique used to obtain adequate information about the structure and dynamics of fluorescent molecules. It is a process, in which the fluorescence intensity of a compound can be decreased by a variety of molecular interactions including excited-state reaction, molecular rearrangement, energy transfer, forming ground state complex and collisional quenching [20–24]. Stern–Volmer plots of certain quenching reactions results static, dynamic or both static and dynamic quenching mode. The main reason for the static quenching is the formation of a non-fluorescent complex between the fluorophore and the quencher in the ground-state, however, the dynamic quenching mode is either due to the presence of two fluorophores with different accessibility to the quencher and/or due to the occurrence of the reverse reaction in the photochemical system [25]. In general, both static and dynamic quenching modes require molecular contact between the fluorophore and quencher. The formation of non-fluorescent ground-state complex between the fluorophore and the quencher results in static quenching and if there is a collision between subsequent formation of a transient complex between excited state fluorophore and a ground-state quencher then dynamic quenching takes place. Thus the difference between the static and dynamic

quenching is the sequence of excitation and complex formation, while the physical bases of two quenching mechanisms are the same.

Static and dynamic quenching can also be distinguished by their differing dependence on temperature and viscosity, or preferably by lifetime measurements [24]. Higher temperatures result in faster diffusion and hence large amounts of collisional quenching. Higher temperature will typically result in the dissociation of weakly bound complexes and hence smaller amounts of static quenching. The fluorescence spectra of ZnO QDs-bromothymol blue are shown in Fig. 5. It is obvious that the fluorescence intensity of ZnO QDs decreases regularly with increasing concentration of bromothymol blue ($0.1\text{--}100 \mu\text{mol l}^{-1}$) but no wavelength shift on the peak occurred. Furthermore, the quenching efficiency of bromothymol blue on ZnO QDs fluorescence was tested using $0.1\text{--}100 \mu\text{mol l}^{-1}$ bromothymol blue at different temperatures, as Fig. 6 showed. It is observed that the Stern-Volmer plot shows a straight line, which is suggested that the fluorophores are a single class and all equally accessible to quencher and the quenching is ascribed to a pure quenching mode. In addition, the slopes increase with increasing temperature, according to the above discussions the quenching mode being present in the quenching mechanism is the pure dynamic [24].

On the other hand, the quenching mode can be concluded from the value of the quenching rate constant, known as K_q . According to the classical Stern-Volmer law, the relationship between quenching efficiency (F_0/F) and the concentration of quencher ($[Q]$) for the complete static or dynamic quenching mode should satisfy the following equation:

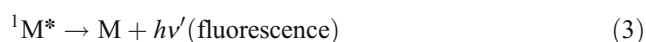
$$F_0/F = 1 + K_{SV}[Q] = 1 + K_q\tau_0[Q] \quad (1)$$

where F_0 and F is the fluorescence intensity of fluorophore in the absence and in the presence of quencher, respectively, $[Q]$ the concentration of quencher, K_{SV} the Stern-Volmer constant corresponding to the slope of the plot for F_0/F vs $[Q]$ in 1 mol^{-1} , K_q the quenching rate constant for bimolecular quenching in $1 \text{ mol}^{-1} \text{ s}^{-1}$, and τ_0 the average fluorescence lifetime of fluorophore without quencher. If the quenching is dynamic, the Stern-Volmer constant K_{SV} will be represented by K_D , i.e. $K_D = k_q\tau_0$. Intuitively, it is useful to note that K_D^{-1} is the quencher concentration at which $F_0/F=2$ or 50% of the intensity is quenched. The

Table 1 The dynamic quenching constant of ZnO-bromothymol blue

Temperature ($^{\circ}\text{C}$)	$K_q/10^{10}$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)	Square of Linear coefficient (r^2)
20	1.55 ± 0.01	0.994
30	2.04 ± 0.01	0.998
40	2.44 ± 0.01	0.997
50	3.79 ± 0.02	0.999

value of K_D can be easily calculated of 1.55×10^5 at room temperature. It was reported that the exciton radiative-lifetime of ZnO nanocrystal was proposed at ten microseconds level [26] as for the nanocrystals with the size less than 5.0 nm [27]. The quenching constant K_q can be calculated from the slope of Stern-Volmer plot using the equation (1), which was listed in Table 1. The values of K_q for ZnO QDs-bromothymol blue quenching procedure were all at the 10^{10} level, which was also suggested that the fluorescence quenching mode was due to the contact collision controlled by diffusion [28]. The quenching procedure can be expressed simply using the following equations:



Conclusion

ZnO QDs was synthesized simply and characterized by XRD, HRTEM, and spectral methods. The maximum excitation and emission wavelength, the quantum yield, and the quenching effect of bromothymol blue for ZnO QDs were obtained, respectively. It was found that the green fluorescence of ZnO QDs could be quenched by bromothymol blue and the quenching mechanism was ascribed to the dynamic quenching mode initiated by contact collision. The quenching constant was calculated and the quenching procedure was expressed using three simple equations.

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