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Global analysis of quenching of the time-resolved emission of ZnO nanocrystals by adsorbed rhodamine B on the basis of Tachiya theory

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ABSTRACT

Normally dye molecules are adsorbed onto the nanocrystal (NC) surface in dye–NC mixed solution, but it is very unlikely that all dye molecules present in the solution will be attached to NCs. The distribution of dye molecules on the NC surface is an important factor to take into account while investigating the quenching of NC emission via energy transfer to adsorbed dye molecules. Here, we analysed time-resolved fluorescence data of ZnO NCs in the presence of rhodamine B (RhB) using Tachiya theory, which assumes the Poisson distribution of dye molecules among the NCs. Energy transfer rate from NC to a dye molecule was found to be much faster than the intrinsic fluorescence decay rate of NCs and fluorescence quenching rate due to intrinsic trap states present in the NC. The association constant was also calculated to acquire information on the nature of association of dye molecules with NCs.

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1. Introduction

Excitation energy transfer (ET) is an important non-radiative interaction between fluorescent chromophores and resulted into fluorescence quenching. The process has recently been utilized for engineering energy flows in quantum dot assemblies [1,2] estimating the efficiency of carrier multiplication in semiconductor nanocrystals [3] and to realize single-molecule optoelectronic switches with single nanocrystal–dye combination [4]. A number of studies [5–15] have shown that the reason for quenching of nanocrystal fluorescence in NC–dye assembly is ET, but the detail whereabouts of the process is not yet completely understood.

Recently, we reported quenching of the defect emission of ZnO nanocrystals by rhodamine B dye [16]. The quenching of ZnO emission was explained on the lights of energy transfer from excited nanocrystal to adsorbed dye molecules and data was analysed under Förster formalism. Guided by previous reports [17,18], it was assumed that all acceptor molecules present in the solution was adsorbed onto the NCs and considered the effect of the n (acceptor/donor) number of acceptors on the fluorescence intensity and lifetime of a single NC. The following equations were used to estimate energy transfer rates:

$$\frac{1}{\tau_{DA}} = \frac{1}{\tau_D} + nk_T \quad (1)$$

$$k_T = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6$$

here τ_D and τ_{DA} are the fluorescence lifetimes of the donor in the absence and presence of the acceptor, respectively. n is the average number of acceptors adsorbed to each ZnO NC. R_0 represents the Förster distance, which is nothing but the distance at which the energy transfer rate become equal to the fluorescence decay rate of only donor. r is the average donor–acceptor distance for the donor–multi–acceptors assembly.

Although, we assumed on an average n number of dye molecules was adsorbed to each ZnO NC, but more generalized treatment would be, to consider the distribution of numbers of dye molecules attached to one NC. While considering the distribution of numbers of dye molecules attached to one NC, it is important to note that among dye molecules introduced in solution, only a part of them are attached to NCs and the remaining are in the solution phase. The distribution of numbers of dye molecules attached to one NC is theoretically shown by Tachiya [19] to obey a Poisson distribution. Moreover, intrinsic trap states due to structural defects are very likely to be present in the NCs and therefore, it is also important to consider the effect of intrinsic traps. According to accumulated knowledge on statistics in similar situations, it is likely that the distribution of numbers of intrinsic traps in one NC also obeys a Poisson distribution. On the basis of these assumption, Sadhu et al. [9,20] analysed the quenching of NC emission by

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adsorbed dye molecules by using the Tachiya theory for fluorescence quenching in micelles [21]. Beane et al. [13] used the same model to explain the energy transfer from NCs to adsorbed dye molecules. Herein, we present theoretical analysis of the experimental results already published in our previous article [16]. We focus for the first time, on a global analysis of the quenching of emission kinetics of ZnO NCs in the presence of RhB using Tachiya theory. Fitting of time-resolved emission of ZnO NCs globally, provided a universal set of values (independent of dye concentration) for rate constants and association constant.

2. Materials and methods

Analytical grade zinc acetate dihydrate, $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$ (extra pure) from Merck, Germany, absolute ethanol (99.9% AR) from S D Fine-Chem Limited and 25% solution of tetramethyl ammonium hydroxide (TMAOH; 25 wt%) in methanol from Loba Chemie Private Limited were used without purification for the synthesis of ZnO NCs. Detail synthesis of ZnO NCs was described in our previous paper [16]. In brief, a solution was prepared by dissolving zinc acetate dihydrate (0.955 g) into absolute ethanol (100 ml). 2.8 ml of tetramethyl ammonium hydroxide solution in methanol (25% w/w) was then injected into the zinc acetate dihydrate solution for the nucleation and growth of ZnO NCs. Prepared ZnO NCs were preserved in a freezer at -4°C until use to avoid increment in particle size due to aggregation. Concentration of the NC dispersion was estimated considering the uniform size distribution of the crystals and complete conversion of precursor materials into the NCs. Spectroscopic grade methanol ($\geq 99.9\%$) and rhodamine B from Sigma–Aldrich were used for all spectroscopic measurements.

UV–vis absorption and emission spectra were recorded using a Shimadzu UV-2450 spectrophotometer and Cary Eclipse fluorescence spectrophotometer (Agilent Technologies), respectively. All samples were excited using 325 nm light. Fluorescence decay kinetics were measured using a time-correlated single photon counting (TCSPC) setup from Photon Technology International (PTI). All samples were excited by 340 nm Nano LED (light emitting diode) light source and monitored at a wavelength of 510 nm. The kinetic traces for the different quencher concentrations were fitted together in MATLAB software with a global set of rate constants using the Nelder–Mead simplex method.

3. Results and discussion

3.1. Steady-state and time-resolved measurements

The average size of synthesized ZnO NCs obtained from high resolution transmission electron microscopy (HRTEM) measurements is $\sim 3.5 \pm 0.5$ nm, as mentioned elsewhere [16]. Fig. 1 shows the absorption and emission spectra of ZnO NCs in methanol. While absorption spectra has a sharp excitonic peak at 314 nm, emission is relatively broad having maximum at 505 nm. It should be noted that the emission of ZnO NCs does not arise due to exciton recombination, rather associated with the recombination of electron–hole pairs present in the multiple low-lying defect states [22–27].

Dye absorption shown in Fig. 1 has a large overlapping with the emission band of NCs. Fig. 2 depicts the changes in the emission spectra of ZnO NCs in the presence of RhB. It is clear from the figure that NC emission is quenched with the addition of RhB and at the same time a new emission band is formed around 570 nm. This newly formed band resembles the emission band of RhB, which is shown in the inset of Fig. 2. The quenching of the fluorescence of ZnO NCs by RhB was explained to occur as a result of energy transfer from photoexcited NCs to adsorbed dyes [16]. Electron

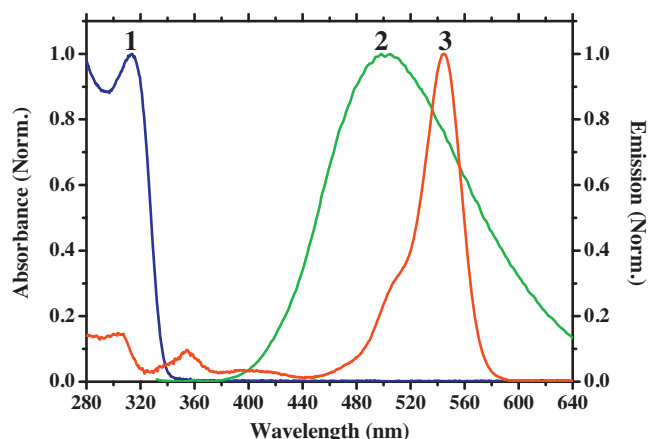


Fig. 1. Normalised absorption (curve 1) and emission (curve 2) spectra of ZnO NCs along with normalised absorption spectra of RhB (curve 3) in methanol.

transfer from NCs to dye molecules can also cause the quenching of NC fluorescence, but in that case concomitant emission from dye would not be observed.

Fluorescence decay kinetics of ZnO NCs in the presence of RhB were measured by TCSPC technique and results are depicted in Fig. 3. Decay traces clearly show quenching of the fluorescence of ZnO NCs by RhB. In our previous study [16], we have shown that the reason for the quenching of fluorescence is energy transfer from ZnO NC to dye molecules. It is apparent from the figure that observed traces are multi-exponential with at least a fast and a slow decay component. Another important feature of the fluorescence decay is that the slope of the traces is the same at long times (>300 ns).

3.2. Analysis of fluorescence kinetics

Tachiya [19,21] developed a model for fluorescence quenching in micellar systems by adsorbed dye molecules. The model assumed the Langmuir adsorption isotherm for the partitioning of dye molecules among micelles and solution, the Poisson distribution of dye molecules among micelles, and the proportionality of the quenching rate constant to the number of adsorbed quenchers. Funston et al. [28] applied essentially the model to

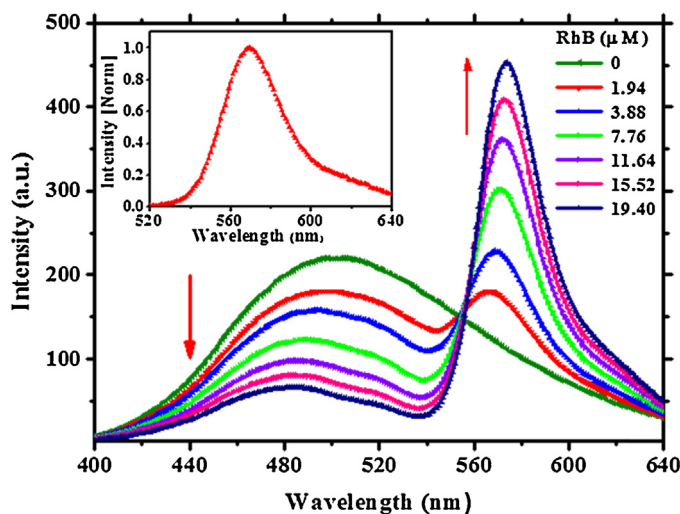


Fig. 2. Emission spectra of ZnO NCs ($1.3 \mu\text{M}$) in the presence of RhB dye in methanol ($\lambda_{\text{ex}} \sim 325$ nm). The concentration of dye varies from 0 to $19.40 \mu\text{M}$. Inset: normalised emission spectra of RhB dye in methanol.

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