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Role of decoupled defect transitions of ZnO nanocrystals in energy transfer

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ABSTRACT

We examine the quenching of the visible emission of zinc oxide (ZnO) nanocrystals (NCs) in the presence of Rhodamine B (RhB) molecules. Spectroscopic measurements reveal that the quenching is nonuniform over the entire emission envelope and this quenching could be explained by the energy transfer from NCs to RhB molecules under Förster formalism. Analysis of the steady state and time-resolved emission data of ZnO NCs demonstrate that at least three defect transitions are associated with the visible emission of ZnO NCs. These transitions are completely decoupled and thereby interact individually with the RhB molecules resulting in wavelength dependent energy transfer and hence uneven quenching of the NC fluorescence. Moreover, we determine the parameters for fluorescence resonance energy transfer (FRET) from NCs to RhB molecules.

1. Introduction

Semiconductor nanocrystals (NCs), because of their unique electronic and photophysical properties engage themselves in fluorescence resonance energy transfer (FRET) with other fluorophores [1–6]. NC-based FRET has attracted immense research interest in recent years due to its utility in sensors [7,8], labelling of biomolecules [9,10], lasers [11], light-emitting diodes [12] and solar energy harvesting [13,14]. The ultrahigh surface to volume ratio of NCs of few nm sizes allow many organic molecules (energy donors or acceptors) to adsorb onto the surface of a single NC and thereby increase the efficiency of FRET [2].

Zinc oxide (ZnO) is a naturally occurring semiconductor having a direct band gap (3.37 eV) and large excitonic (electron–hole pair) binding energy (60 meV). ZnO NCs have received a lot of industrial attention because of easy synthesis, low cost, nontoxicity, chemical stability [15] and broad emission in the UV and visible range [16]. The broad visible emission whose origin is still a matter of debate [17,18] makes it very special in FRET studies. It is well accepted that the emission of ZnO NCs in the visible wavelength region is associated with low-lying radiative trap states that are formed due to either intrinsic or extrinsic defects [19,20]. Although, a large number of reports [3,5,21,22] have shown quenching of the excitonic emission of semiconductor NCs due to FRET, studies on the involvement of the defect transitions in energy transfer (ET) are scarce. In few previous reports [14,15,23–25], the quenching of the defect emission of ZnO NCs was explained using FRET mechanism. Makhal et al. [14] not only showed FRET from ZnO NCs to ruthenium based dye N719 but also pointed out the consequence: significant enhancement of the short circuit current of the dye sensitized solar cells made of these NC-dye combination. Recently, a kinetic model proposed by Tachiya [22] was employed to interpret the energy transfer from ZnO NCs to organic molecules [26]. Although, a number of groups [15,25] proposed the association of more than one distinct defect states to the visible emission of ZnO NCs, reports [26–28] are there which demonstrated that the entire defect emission of ZnO NCs arises from a single electronic transition coupled to the phonon modes of the crystal lattice and hence behaves like a single fluorophore emission. Furthermore, how many defect transitions of NCs take part in the energy transfer process with organic molecules is still controversial. While Beane et al. [26] found energy transfer from ZnO NCs to RhB molecules due to interaction of RhB with single defect transition, Pal and coworkers suggested interaction with two distinct defect transitions.

Herein, we explore the quenching of visible emission of ZnO NCs in the presence of Rhodamine B molecules employing both steady state and time-resolved spectroscopic techniques. Spectroscopic measurements demonstrate that the quenching of NC emission is due to FRET from NCs to RhB molecules and therefore data are analyzed under FRET formalism considering NC is acting as an

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energy donor to adsorbed RhB molecules that behave like multiple acceptors to the NC surface. The observed wavelength dependent quenching of the NC fluorescence is successfully explained using Förster mechanism establishing the fact that at least three distinct defect transitions are responsible for the entire visible emission of ZnO NCs and all of them interact independently with the transition dipole of the RhB molecules yielding different ET efficiencies (or rates).

2. Experimental

2.1. Materials

Analytical grade chemicals were used without further purification for the synthesis of NCs. Zinc acetate dehydrate, $(CH_3COO)_2Zn{\cdot}2H_2O$ (extra pure) from Merck, Germany, absolute ethanol (99.9% AR) from S D Fine-Chem Limited and 25% solution of tetramethyl ammonium hydroxide (THAOH; 25 wt%) in methanol from Loba Chemie Private Limited were used for the synthesis. In spectroscopic studies, Rhodamine B (RhB) and Quinine from Sigma–Aldrich was used. All spectroscopic measurements were carried out in methanol (spectroscopic grade) as received from Sigma–Aldrich. The details of the synthesis and characterization of ZnO NCs are discussed in the following sections.

2.2. Synthesis of ZnO NCs

ZnO NCs were synthesized via the chemical method proposed by Wood et al. [29]. In brief, 0.955 g zinc acetate dihydrate was added in 100 ml absolute ethanol and heated up for proper dissolution by forming a clear solution. After complete dissolution, 2.8 ml of 25% (w/w) tetramethyl ammonium hydroxide in methanol was injected with constant injection rate into it under vigorous stirring condition in a water bath at room temperature. Fast and constant injection rate was maintained for the nucleation of uniform small size NCs. Solution of ZnO NCs thus prepared was kept at −4 °C in a freezer until use to avoid further growth in particle size due to aggregation. Concentration of the nanoparticles solution was determined by assuming the uniform size distribution of the particles and complete conversion of precursors into NCs.

2.3. Spectroscopic techniques

UV–visible absorption and fluorescence (and excitation) spectra were recorded using a Shimadzu UV-2450 spectrophotometer and Cary Eclipse fluorescence spectrophotometer (Agilent Technologies), respectively. All samples were excited at 325 nm for fluorescence and monitored at 570 nm for excitation spectra recording. A high resolution transmission electron microscope (HRTEM, JEOL Model 2100 X) was used to characterize the NCs and estimate their size.

Fluorescence quantum yield (QY) of ZnO NCs was estimated by comparing its total fluorescence intensity under the entire emission envelope with that of the standard quinine sulfate in 0.5 M H_2SO_4 solution ($\Phi_f^s = 0.546$) [30] considering the following relation

$$\Phi_f^i = \frac{F^i f_s n_i^2}{F^s f_i n_s^2}\Phi_f^s \tag{1}$$

where Φ, F, f and n represent QY, integrated fluorescence intensity (i.e. area under the fluorescence spectrum), absorption factor and refractive index, respectively. *i* and *s* stands for sample and standard or reference.

Time-resolved fluorescence measurements were carried out using Nano LED based time-correlated single photon counting (TCSPC) setup from Photon Technology International (PTI) and Fluorohub from HORIBA JobinYvon. Fitting of decay curves was done with nonlinear least square fitting algorithm using the following equation,

$$I(t) = b + \sum_{i=1}^{n} \alpha_i \exp\left(\frac{-t}{\tau_i}\right) \tag{2}$$

Here b is the baseline correction ("dc" offset) or background, n is the number of discrete emissive species, α_i is the pre-exponential factor and τ_i is the fluorescence lifetime associated with the ith decay component. The amplitude weighted average lifetime for multiexponential decay can be expressed as follows [31]

$$\langle \tau \rangle = \sum_{i=1}^{n} A_i \tau_i \tag{3}$$

where $A_i = \alpha_i / \Sigma\alpha_i$ is the fractional contribution of the ith decay component.

According to Förster theory [31,32], the rate of energy transfer for an isolated single donor–acceptor system separated by a distance r from the centre of their transition dipoles is given by

$$k_T(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 \tag{4}$$

where τ_D is the fluorescence lifetime of the donor in the absence of the acceptor and R_0 is known as the Förster distance, the distance at which the energy transfer rate is equal to the fluorescence decay rate of the donor in the absence of the acceptor. Förster distance (R_0) was calculated from the equation

$$R_0 = 9.78 \times 10^3 \left[\kappa^2 n^{-4} Q_D J(\lambda)\right]^{1/6} \text{ Å} \tag{5}$$

where κ^2 describes the relative orientation of the transition dipoles of the donor and the acceptor in space and usually for randomize motion, it is assumed to be 2/3, n is the refractive index of the medium, Q_D is the quantum yield of the donor in the absence of the acceptor. $J(\lambda)$ represents the spectral overlap between the donor emission (normalized to unit area) and acceptor absorption and was determined by using the following expression.

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)d\lambda} \quad \text{mol}^{-1}\text{cm}^{-1}\text{nm}^4 \tag{6}$$

where $F_D(\lambda)$ is the fluorescence intensity of the donor in the wavelength range λ to $\lambda + d\lambda$, $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at wavelength λ and expressed in units of $M^{-1}\ cm^{-1}$ when λ is in nanometre (nm).

In the case where a single donor is surrounded by several acceptors, the FRET efficiency (E) for these complex interactions can be defined as [33]

$$E = \frac{nR_0^6}{nR_0^6 + r_n^6} \tag{7}$$

where n is the acceptor/donor ratio or discrete number of acceptors around a donor and r_n is the average donor–acceptor distance for the donor–multi-acceptors assembly. For each n the donor–acceptor separation was estimated by the relation

$$r_n = R_0\left(\frac{n(1-E)}{E}\right)^{1/6} \tag{8}$$

Efficiency of FRET was determined experimentally from both steady state and time-resolved fluorescence data using these expressions

$$E = 1 - \frac{F_{DA}}{F_D} \quad \text{(for steady state)} \tag{9}$$