Non-linear effects in the quenching of fluorescent quantum dots by nitroxyl free radicals

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Quenching of quantum dot luminescence by nitroxides is extremely non-linear and dependent on nanoparticle size, being most effective for the smaller particles; it is proposed to involve an electron exchange mechanism.

Nanoparticles, and in particular semiconductor quantum dots (QD), have been the subject of intense study;[1,2] their tunable narrow band emission and broad absorption makes them attractive for numerous imaging and sensing applications. We are interested in their interactions with paramagnetic species, such as free radicals and their eventual use in functional materials; in this study we have examined the quenching of CdSe QD (purchased from Evident, coated with TOPO, trioctylphosphine oxide) by the paramagnetic species TEMPO (2,2,6,6-tetramethyl-piperidine-*N*-oxide free radical) in toluene solution at room temperature. We believe that QD emission quenching by free radicals and its size dependence has not been studied before.

Quenching of QD emission can be performed with one-size or mixtures of QD of different sizes by monitoring intensity changes of their characteristic emission bands for different concentrations of quencher. The intrinsic properties of nanocrystals are strongly size-dependent.[1,2] In our case we use QD of 2.4 nm (green, λ_{max} 525 nm), 3.2 nm (orange, λ_{max} 575 nm) and 6.7 nm (red, λ_{max} 630 nm), in diameter. The emission spectra of the two smaller ones in the absence and presence of selected concentrations of TEMPO (excitation at 380 nm) are shown in Fig. 1. Note a small red shift at high TEMPO concentrations.

From Fig. 1 it is evident that the smaller particles are quenched more efficiently than larger ones (note the more facile quenching of the short wavelength band). This is also reflected when the data (based on the fluorescence intensity at the maximum) is plotted in a Stern–Volmer fashion, as shown in Fig. 2. The pronounced non-linearity observed explains the spectral shift observed in Fig. 1. Each band arises from a distribution of nanoparticle sizes. Since small particles are quenched more effectively than large ones, the surviving emitting population is enriched in larger nanoparticles. Similar non-linear behaviour was recently reported in the quenching of QD by cyanide ions.[3]

Fig. 2 is characterized by remarkable non-linearity. Typical Stern–Volmer plots are linear; deviations from linearity are frequently attributed to quenching of more than one electronic state, or to a combination of static and dynamic quenching. However, the changes in the slopes, particularly for the smaller QD are just too large to adapt to a simple two-state or two-modes of quenching model. We observe an exponential dependence (see Fig. 2, insert B), according to eqn. (1).

$$\frac{I_0}{I} = e^{\alpha[\mathrm{TEMPO}]} \qquad (1)$$

The values of α obtained from the fits of insert A and B in Fig. 2 are 1.6, 6.4 and 13.7 M^{-1} for large, medium and small dots, respectively. The size—and thus band gap—dependence is so pronounced that multiple quenching plots can be recorded by monitoring the quenching at the maximum and on the sides of the emission band, as shown in Fig. 3 (top), where plots for (nominally) 2.4 nm QD were obtained at 510, 525 (max) and 540 nm. This allows the detailed determination of the parameter α dependence with the emission wavelength (and thus band-gap and size), as shown in Fig. 3 (bottom). Independent EPR experiments suggest that there is no specific binding between TEMPO and the QD; thus in a solution of TEMPO (2×10^{-5}M) the *N* coupling constant (1.55 ± 0.01 mT)[4] line width and amplitude remain unchanged upon addition of an equimolar amount of green QD.[5]

A dependence of the type shown in Fig. 2 is expected in several related models, including a simple Perrin model,[6] in which only immobile[7] quenchers within a certain radius are effective, as well as models such as distance-dependent quenching (DDQ)[8] and others[9] that take into account time-dependent terms usually neglected in Smoluchowski's equation.[9,10] Observation of an exponential

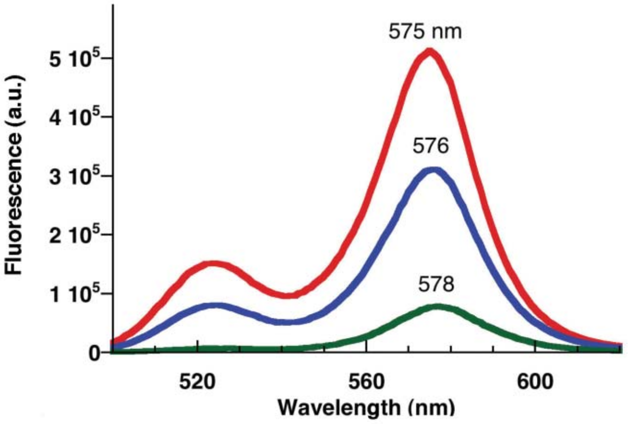

Fig. 1 Fluorescence spectra (λ_{ex} 380 nm) of a toluene solution of 2.4 and 3.2 nm QD with the same dot concentrations (3.7 μM). Fluorescence intensity is decreasing as the concentration of TEMPO is increased: 0 M, 0.04 M, 0.2 M TEMPO.

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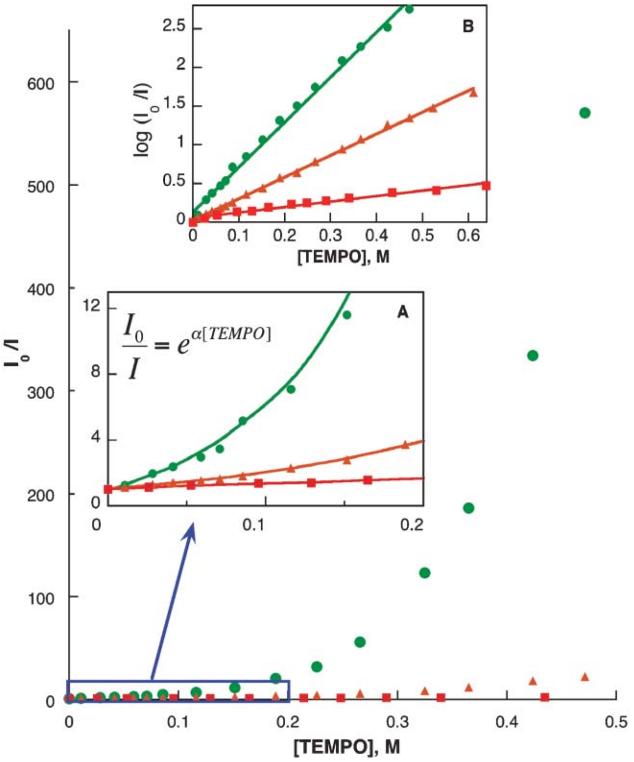

Fig. 2 Fluorescence intensities at the maximum for each size QD shown as a Stern–Volmer plot. I_0 is the maximum of fluorescence without TEMPO. Data for QD of diameter 2.4 (green), 3.2 (orange) and 6.7 nm (red). Insert A shows an enlargement for [TEMPO] < 0.2 M, and insert B a plot based on the logarithm of the Stern–Volmer-type data. The data were corrected to account for competitive absorption by TEMPO at the excitation wavelength (380 nm).

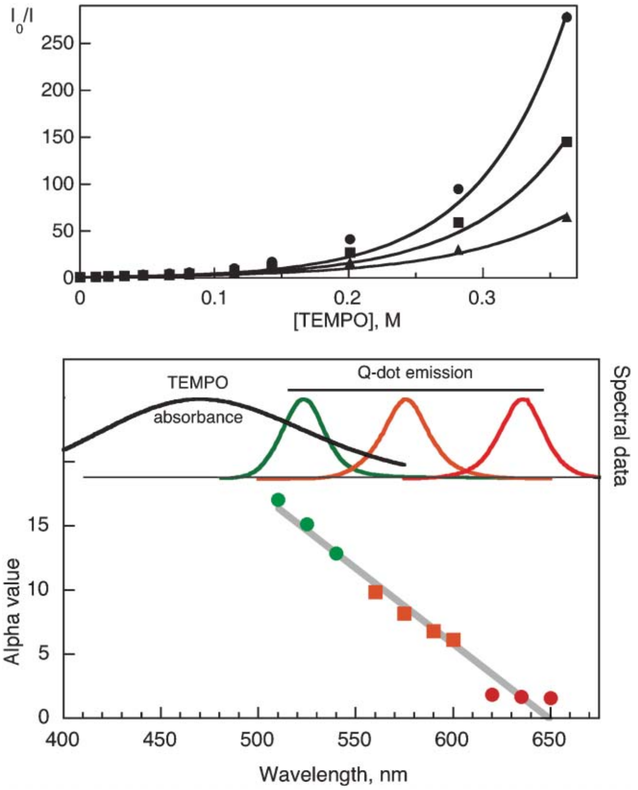

Fig. 3 Top: Stern–Volmer plots of a toluene solution of QD 4.1 μM at 510 nm (•) 525 nm (■) and 540 nm (▲); the data were corrected to account for competitive absorption by TEMPO at the excitation wavelength (380 nm). Bottom: Linear fit of α *vs.* wavelength. The α values were derived from the fits of Stern–Volmer plots to eqn. (1). Data points represent α for green (•) and orange (■) and red (•) quantum dots at different wavelengths.

dependence provides a clear relationship between emission and quencher concentration. In CdSe QD, band gap, size and surface curvature are related and can influence quenching processes[11] as well as the access through the organic coating to the semiconductor surface.[1,2] Interestingly, in a simple Perrin analysis (*i.e.*, $\alpha = N_A V$, where N_A is Avogadro's number and V the quenching volume), the calculated radii (corresponding to 50% quenching efficiency) for quenching are 1.8, 1.5 and 0.9 nm, for particles of 2.4, 3.2 and 6.7 nm in diameter, respectively; notably, for the larger QD the quenching radius is much smaller than the QD size itself. In this case quenching radii is better viewed as the action radius for the quencher as it approaches the QD surface; thus for the smaller (green) QD a TEMPO quencher can almost 'reach' across the nanoparticle, while for the larger QD (*e.g.*, red at 6.7 nm) the quencher can only interact with excitons near the surface, given its quenching radius of only 0.9 nm.

Quantum dots are known to participate in fluorescence resonance energy transfer (FRET),[12] and quenching of organic molecules by nitroxides is known to be influenced by the excited state energy of the donor;[13,14] however, in the cases of the QD studied, the TEMPO absorption (peak at 470 nm) is at higher energy than the band gap for all the QD used; in fact, the overlap integral between the TEMPO weak transition and the QD emission is modest for the green QD and negligible for the others, see spectral data in Fig. 3. The fact that the quenching radii correspond to contact distances argues strongly in favour of an electron exchange mechanism. This may involve a spin relaxation mechanism similar to that in which paramagnetic quenchers interact with triplet biradicals,[15] or the introduction of surface traps in the QD by the half-filled SOMO in the nitroxide. An alternate interpretation also leading to effective quenching would involve electron transfer from the conduction band to the nitroxide (a mild acceptor), and back electron transfer from the nitroxide to the valence band, effectively leading to quenching using the nitroxide SOMO as a shuttle for electron and hole.

Electron exchange requires close proximity with the excited electron in the conduction band and should be favoured for smaller nanoparticles. Surface curvature may also play a role in this interaction; one may speculate that in the case of the smaller nanoparticles the higher curvature causes some opening of the TOPO molecules, thus facilitating the approach of quenchers to the CdSe surface. As already noted, band-gap, size and surface curvature are inseparable quantities for semiconductor nanoparticles.

The size-dependent quenching efficiencies observed may find applications where selective quenching of one colour is desirable, even when QD of multiple colour/sizes are simultaneously present, as in some biological applications. Further, CdSe QD have been recently derivatized with alkoxyamines, as precursors for nitroxide-mediated polymerization, an area where the understanding of QD–nitroxide interaction would be useful.[16]

In summary, an interesting dependence of nitroxide fluorescence quenching with QD size has been observed; the data clearly point to short range electron exchange interactions as the mechanism for quenching. Semiconductor nanocrystals have a strong variation of their quenching properties with their size. These unusual non-linear effects may prove useful in the design of functional materials.

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