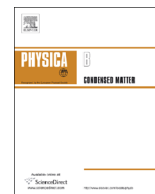




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Quenching of photoluminescence of colloidal ZnO nanocrystals by nitronyl nitroxide radicals



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ABSTRACT

Quenching of the photoluminescence of colloidal zinc oxide nanocrystals by a series of stable nitronyl nitroxide radicals was studied by means of stationary and time-resolved luminescence spectroscopy. Among the studied radicals the most efficient quenchers of the ZnO luminescence are the carboxyl-substituted species. The *meta*-substituted radical was found to be a more active quencher, than *para*-substituted one due to a closer proximity of the radical center to the nanocrystals surface. The PL quenching has a complex dynamic/static character. The dynamic quenching arises from photocatalytic radical reduction by ZnO conduction band electrons, while the static quenching is caused by adsorption of the photoreduction products on the nanocrystal surface. The non-substituted and OH-substituted radicals are inferior to the products of their photoreduction in capability of adsorption of the ZnO surface, and the quenching is dominated by interactions between the nanocrystals and photoreduced hydroxylamines. In case of COOH-substituted radicals, however, the radicals compete with the photoreduction products for the surface sites of ZnO nanocrystals resulting in a dynamic character of photoluminescence quenching.

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1. Introduction

Luminescent semiconductor nanocrystals (NCs) attract considerable and steady interest due to unique size-dependent optical and emission properties and enormous potential of their application in various cutting-edge technologies, such as light-emitting diodes, solar concentrators, luminescent bio-imaging and bio-sensing, etc. [1–4]. As the most commonly used luminescent NCs of cadmium chalcogenides reveal cytotoxicity already on a nanomolar level when used for the in vivo bio-diagnostics, a special interest is turned to much less toxic luminescent nanomaterials, such, for example, as zinc oxide [3–6]. Currently, ZnO NCs are broadly studied as active components of photo- and electroluminescent systems, solar cells, as transparent UV light absorbers, as well as photocatalysts [1,2,5,7,8]. Interaction between ZnO NCs and the cell components, especially under the illumination, can give rise to various reactive radical species resulting in the oxidative stress [3,4]. On the other hand, interactions between semiconductor NCs and radical species generated in the cells have been observed to result in the photoluminescence (PL) quenching enabling luminescent detection of radical species [9–12].

To model pathways of radical species in the cells various persistent nitroxide and nitronyl nitroxide radicals are often used allowing the radical detection either by the electron paramagnetic resonance or by the optical spectroscopy [13,14]. The stable nitroxide radicals are known by their ability to quench the PL of various semiconductor NCs [10,11,13,15,16] and carbon nanoparticles [12], manifesting dependences of the PL quenching efficiency both on the radical structure [13,16,17] and the NC size [13]. At the same time, no papers can be found reporting interactions between stable nitroxide radicals and colloidal ZnO NCs.

Recently, we have reported PL quenching of colloidal ZnO NCs by a stable nitronyl nitroxide radical, 2-(*o*-hydroxyphenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (Nit(*o*-OH)Ph) as well as NC size- and wavelength-dependent photochemical interactions between ZnO NCs and Nit(*o*-OH)Ph resulting in the radical reduction [18]. The present work aims at elucidation of relationships between the structure of nitronyl nitroxide radicals and their ability of quenching the luminescence of ZnO NCs by a combination of stationary and time-resolved PL spectroscopy.

2. Experimental

Commercially available reagents (from Sigma-Aldrich, Fluka) were used without further purification. Ethyl alcohol was dried

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with sodium and diethyl phthalate. Nitronyl nitroxide radicals were synthesized by well-known methods [19] via the steps of precursors formation by condensation of corresponding aldehydes with 2,3-bis(hydroxylamino)-2,3-dimethylbutane and oxidation of the precursors with sodium periodate. In PL quenching experiments various aliquots of 0.001 M solutions of radicals in absolute ethanol were taken and introduced into the ZnO NC colloids. Zinc oxide colloids were prepared similarly to Refs. [18,20,21] via reaction of anhydrous zinc (II) acetate with NaOH in the absolute ethyl alcohol followed by heat treatment at 60 °C for 2 h. In the PL quenching experiments the as-synthesized 0.01 M colloids were diluted by absolute ethanol to 0.001 M. Absorption spectra were registered with a HP Agilent 8453 spectrophotometer. The PL spectra and decay profiles were obtained using an Edinburgh Instruments FLS920 photon counting system. The samples were placed in 1.0 mm quartz cuvettes and excited by a picosecond LED with $\lambda=320$ nm.

3. Results and discussion

Fig. 1a shows the structure of nitronyl nitroxide radicals studied in the present paper and corresponding abbreviations used further to refer to the radicals. Absorption spectra of the radicals (Fig. 1b) reveal an intense band at 300–400 nm corresponding to the allowed $(\pi\pi)^*$ transitions in a conjugated section of the molecules and a weak band

in the visible range, at 500–700 nm corresponding to a combination of various $(n\pi)^*$ transitions involving unpaired electrons of heteroatoms [22]. Introduction of an electron donating OH group results in a shift of the maxima of both bands of Nit(*o*-OH)Ph to shorter wavelength as compared to NitPh (curves 1 and 2), while for Nit(*m*-COOH)Ph and Nit(*p*-COOH)Ph an opposite trend is observed (curves 3 and 4) as a result of conjugation of the carboxyl group with the aromatic system.

Absorption spectrum of colloidal ZnO NCs in ethanol exhibits a continuous band with a sharp edge at ~ 360 nm (Fig. 1c, curve 1). The band gap of ZnO NCs calculated as an intercept of a tangent to the linear section of the band edge and the X-axis, was found to be $E_g=3.47$ eV. The average size d of ZnO NCs was estimated from the band gap using the well-known calibration $E_g(d)$ curves [21] as $d=4.5$ nm. The ZnO NCs emit broadband photoluminescence in the range of 420–750 nm with a PL band center at 530–540 nm (Fig. 1c, curve 2). A large Stokes shift of the PL band maximum and a large spectral band width indicate that PL originates from the radiative electron–hole recombination with the participation of charge carriers localized in deep traps in the band gap [20,23].

Introduction of nitronyl nitroxide radicals into ZnO colloid results in a decrease of the PL intensity proportional to the radical concentration (Fig. 2a) with the band maximum and shape remaining unchanged. The efficiency of PL quenching depends strongly on the radical structure and increases drastically from NitPh bearing no functional groups to the radical with a carboxyl group attached to the *meta*-position of benzene ring. Dependences

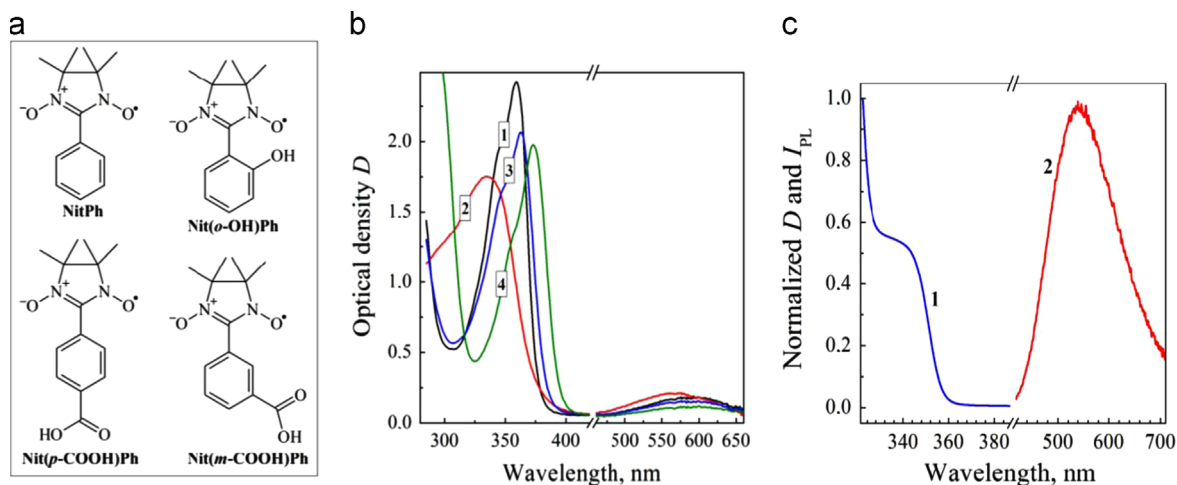


Fig. 1. (a) Structure of the studied nitronyl nitroxide radicals. (b) Absorption spectra of the NitPh (curve 1), Nit(*o*-OH)Ph (curve 2), Nit(*m*-COOH)Ph (curve 3), and Nit(*p*-COOH)Ph (curve 4) in ethanol. Radical concentration is 1×10^{-3} M and cuvette: 1.0 mm. (c) Normalized absorption (curve 1) and PL spectra (curve 2) of ZnO NCs.

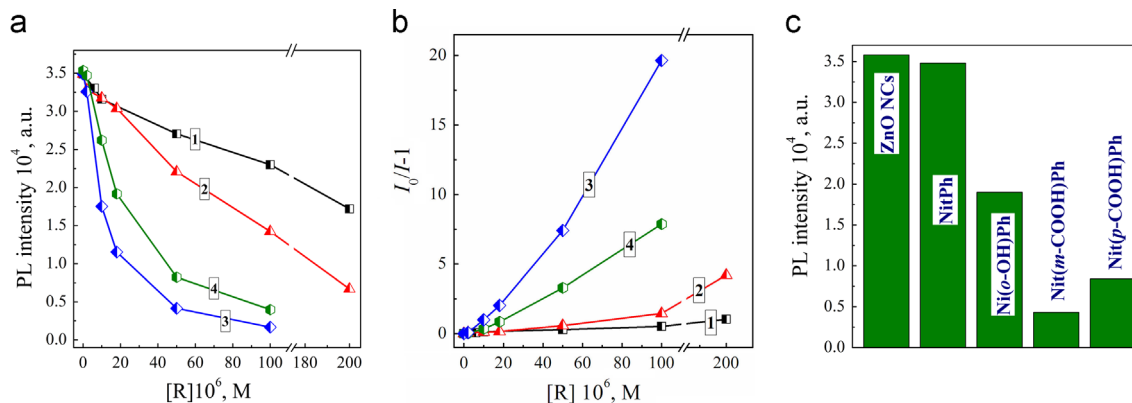


Fig. 2. PL intensity of ZnO NCs I (a) and $I_0/I - 1$, where I_0 is the original PL intensity of ZnO colloid (b) as functions of the molar concentration $[R]$ of NitPh (curve 1), Nit(*o*-OH)Ph (2), Nit(*m*-COOH)Ph (3), and Nit(*p*-COOH)Ph (4). (c) ZnO NC PL intensity in the presence of different nitronyl nitroxide radicals (R) at $[R]=5 \times 10^{-5}$ M and $[ZnO]=2 \times 10^{-3}$ M.

between PL intensity and the radical concentrations are non-linear when plotted in the Stern–Volmer coordinates (Fig. 2b) indicating a complex quenching mechanism with a dominating contribution of the static quenching.

At a low radical concentration (1×10^{-5} M) NitPh almost does not affect the PL intensity of ZnO NCs. Decoration of the NitPh with a functional group leads to a considerable increase in the quenching efficiency (Fig. 2c) and a reduction of the original PL intensity by 47% (Nit(*o*-OH)Ph), 76% (Nit(*p*-COOH)Ph) and 88% in case of Nit(*m*-COOH)Ph. The quencher concentration at which half of the original PL intensity is observed, $[C]_{1/2}$, varies with the radical structure by two orders of magnitude – from 2×10^{-4} M for NitPh to $\sim 8 \times 10^{-5}$ M for Nit(*o*-OH)Ph, 2.5×10^{-5} M for Nit(*p*-COOH)Ph and 1×10^{-5} M for Nit(*m*-COOH)Ph. The behavior of the systems studied here is in general similar to that of other “radical–NCs” systems, for example, “tetramethylpiperidine-N-oxide (TEMPO)–CdSe NCs” [11,13,15], where a strong non-linearity of the Stern–Volmer plots was observed along with a drastic change of the $[C]_{1/2}$ concentration – from 10^{-2} – 10^{-1} M for non-functionalized TEMPO to 10^{-7} – 10^{-3} M for amino-derivatives of TEMPO.

Kinetic curves of the PL decay of colloidal ZnO NCs in ethanol are strongly non-exponential (Fig. 3a, curve 1) and can be fitted with a linear combination of at least four exponents $I(t) = \sum_i A_i e^{-t/\tau_i}$, where $I(t)$ is the PL intensity, $i=1,0,4$, A_i and τ_i are the fitting variables. An average radiative ZnO NC life-time calculated from τ_i as $\langle \tau \rangle = \sum_i (A_i \tau_i^2) / \sum_j (A_j \tau_j)$ [24] was found to be as large as 1380–1400 ns, which is typical for deep-trap-mediated radiative electron–hole recombination in colloidal ZnO NCs [23,25].

Introduction of the nitronyl nitroxide radicals results in acceleration of the PL decay (Fig. 3a, curves 3–5) and a corresponding decrease of the average life-time (Fig. 3b) the decrease magnitude depending on the radical structure. The radicals can be divided into two groups by their influence on $\langle \tau \rangle$ (Fig. 3b). The NitPh and Nit(*o*-OH)Ph (Fig. 3b, curves 1 and 2) affect the life-time at a low concentration, $[C] \ll 2 \times 10^{-5}$ M, decreasing the $\langle \tau \rangle$ by 15% and $\sim 30\%$, respectively. At a higher radical concentration $\langle \tau \rangle$ remains virtually unaffected in a broad concentration range indicating pure static PL quenching mechanism in such conditions. In case of carboxylated Nit(*m*-COOH)Ph and Nit(*p*-COOH)Ph radicals (Fig. 3b, curves 3 and 4) a strong influence of the radicals on the radiative life-time of ZnO NCs is observed, the $\langle \tau \rangle$ decreasing sharply in the range of $[C] \ll 2 \times 10^{-5}$ M and more smoothly at a higher radical concentration. At $[ZnO] = 2 \times 10^{-3}$ M and the NC size $d=4.5$ nm the radical concentration of 2×10^{-5} M roughly corresponds to ~ 20 radical molecules per nanocrystal. Similarly to the PL quenching, by their influence on the radiative life-time of ZnO NCs the radicals studied can be

arranged in the following sequence: NitPh \ll Nit(*o*-OH)Ph \ll Nit(*p*-COOH)Ph \ll Nit(*m*-COOH)Ph (Fig. 3c).

The described results clearly show that one of the major factors affecting the efficiency of PL quenching of ZnO NCs is the chemical functionality of the radical enabling its anchoring to the NC surface. The NitPh radical that has no functional groups able to interact strongly with the surface of ZnO NCs has the smallest effect of the PL intensity. The PL quenching efficiency increases considerably as NitPh is functionalized by a hydroxyl group and transformed into Nit(*o*-OH)Ph. A much stronger effect is caused by NitPh with a carboxyl group capable to tight binding to the surface of ZnO NCs. The time-resolved data shows that the dominant mechanism of quenching changes as well, switching from static quenching to predominantly dynamic quenching. Between two similar carboxyl-decorated radicals, Nit(*p*-COOH)Ph and Nit(*m*-COOH)Ph, it is the *meta*-substituted moiety that is a stronger quencher of the ZnO NC luminescence. The most probable reason for that is a closer proximity of the radical center to the ZnO NC surface in case of radical conjugation via the *m*-COOH as compared to *p*-COOH. Similar effects of the distance between the NC surface and the radical center on the PL quenching efficiency were observed in Ref. [16] for TEMPO family radicals with different substitutes. A significant difference between the results reported here and in Ref. [16] is that in Ref. [16] the PL quenching activity of TEMPO derivatives with various substitutes possessing different size and different nature was compared, while here the effect of the distance between the radical center and the NC surface can be observed for two radicals of identical chemical composition differing only in the molecule geometry.

In our recent work on the “ZnO NC–Nit(*o*-OH)Ph” system [18] it was shown that illumination of ZnO NCs by UV light that is in conditions similar to those of the present work the radical is reduced by the photogenerated ZnO conduction band electron to a corresponding hydroxylamine. Similar effect of photoreduction of TEMPO derivatives by CdSe NCs in toluene was observed in Ref. [16]. Typically, the PL intensity of semiconductor NCs increases sharply when a nitroxide radical quencher is reduced to a corresponding hydroxylamine and the radical species sensing technique is based on the effect of reversible NC PL quenching [10,11,13,16,17,26]. In case of the present ZnO NCs with no additional capping agents on the NC surface, the products of radical reduction remain adsorbed on the surface resulting in permanent PL quenching. The capability of reduced form of the nitronyl nitroxide radicals to quench the ZnO NC PL was shown by us in Ref. [18] on the example of Nit(*o*-OH)Ph radical.

Overall, the quenching of ZnO NCs by the nitronyl nitroxide radicals originates from both the conduction band electron

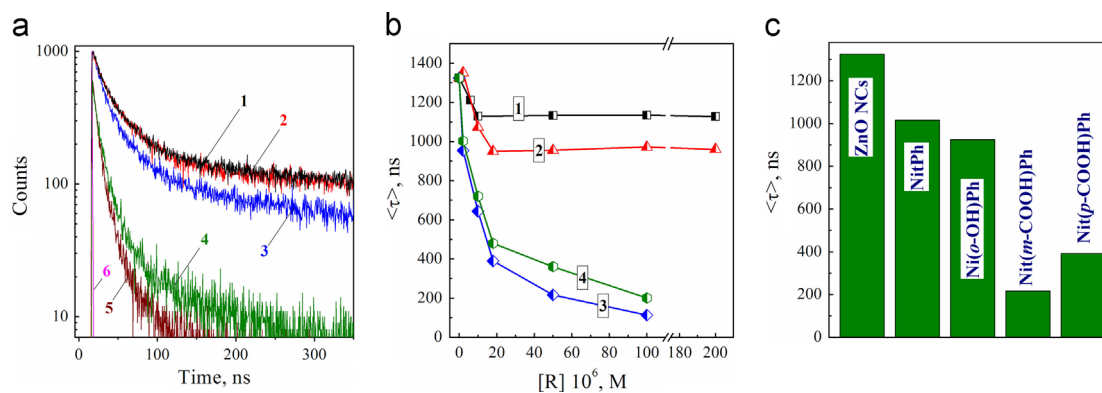


Fig. 3. (a) Kinetic curves of PL decay for ZnO NCs without radical additives (curve 1) and in the presence of 2×10^{-6} M (2), 1×10^{-5} M (3), 5×10^{-5} M (4), and 1×10^{-4} M Nit(*m*-COOH)Ph (5). Curve 6 is an instrument response function (IRF). (b) Average ZnO NC PL life time (τ) as a function of concentration of NitPh (curve 1), Nit(*o*-OH)Ph (2), Nit(*m*-COOH)Ph (3), and Nit(*p*-COOH)Ph (4). $[ZnO] = 2 \times 10^{-3}$ M. (c) Average ZnO NC PL life time in the presence of different nitronyl nitroxide radicals at $[R] = 5 \times 10^{-5}$ M and $[ZnO] = 2 \times 10^{-3}$ M.

consumption in the photocatalytic reduction of the radical and interactions between ZnO NCs and the product of the photochemical reaction. At a concentration higher than $(1-2) \times 10^{-4}$ M the absorbance of the radicals at $\lambda = 320$ nm becomes comparable with that of zinc oxide and a light screening effect of the radicals can be expected additionally decreasing the PL intensity ZnO NCs. The differences in the PL quenching efficiency arise mainly from a different character of radical interaction with the ZnO NC surface and a different rate of photochemical reduction. The NitPh has no functionalities capable to interact with the NC surface and the rate of NitPh photoreduction is low and, therefore, PL quenching is inefficient. However, the product of the photoreduction, NitPhH, adsorbs much better on the NC surface and suppresses the radiative electron-hole recombination resulting in the static character of the PL quenching. The mostly dynamic character of PL quenching at a low radical concentration, at $[\text{NitPh}] \ll 1-2 \times 10^{-5}$ M, probably reflects the fact that in such conditions the photocatalytic process is not efficient, the concentration of reduced NitPhH is very low and, overall, the PL quenching efficiency is determined by diffusion of NitPh to the NC surface. Increase in the radical concentration accelerates the photocatalytic reduction of NitPh to hydroxylamine which remains adsorbed on the NC surface resulting in the static PL quenching.

Essentially the same, but more pronounced, tendency is observed for Nit(*o*-OH)Ph radical, which also concedes to the reduced form, Nit(*o*-OH)PhH in capability to adsorb on the ZnO NC surface. Evidently, in case of the COOH-substituted radicals, both the starting species and the products of their photocatalytic reduction have more or less equal capability of adsorption on the NC surface, mostly via the carboxyl group, and the competition between the oxidized and reduced forms of the quenchers allows for continuous supply of fresh portions of the radical species, thus resulting in a partially dynamic character of the PL quenching in the entire studied range of radical concentration. At the same time, static PL quenching also occurs by the products of photocatalytic radical reduction adsorbed on the ZnO NC surface.

4. Conclusions

Among the studied nitronyl nitroxide radicals the most efficient quenchers of the ZnO NC luminescence are the carboxyl-substituted species. For such radicals, more efficient quenching is achieved for the *meta*-substituted compound, as compared to *para*-substituted radical, due to a closer proximity of the radical center to the NC surface. The PL quenching has a complex dynamic/static character. The dynamic quenching arises from consumption of the photogenerated ZnO conduction band electron in the photocatalytic radical reduction, while the static quenching is caused by adsorption of the photoreduced products on the NC surface. The non-substituted and hydroxyl-substituted radicals are inferior to the products of their photoreduction in capability of adsorption of the ZnO NC surface, and, therefore, the quenching is dominated by interactions between the NCs and

photoproducted hydroxylamines and has a clearly static character. In case of carboxyl-substituted radicals, however, the radicals compete with the photoreduction products for the surface sites of ZnO NCs resulting in a predominantly dynamic character of PL quenching.

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