# Comment on "Giant exciton-light coupling in ZnO quantum dots" [Appl. Phys. Lett. 81, 748 (2002)]

Vladimir A. Fonoberov[a] and Alexander A. Balandin
*Nano-Device Laboratory, Department of Electrical Engineering, University of California—Riverside, Riverside, California 92521*

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In a recent letter,[1] Gill and Kavokin reported calculation of the radiative lifetime in ZnO quantum dots (QDs), which took into account the retardation effects. The main result of their work was that the radiative lifetime $\tau_r$ reaches a minimum of 264 ps for a ZnO QD with radius 16.7 nm. The authors have concluded that it is significantly smaller than for CdSe or InGaAs QDs and demonstrates "a huge coupling of the electronic states with the electromagnetic field" in ZnO QDs.

The accurate knowledge of the radiative lifetime in ZnO QDs acquires importance due to recent progress in fabrication of ZnO nanostructures and their proposed applications in optoelectronic devices. The reported value for the radiative lifetime of bulk ZnO, measured using the time-resolved photoluminescence spectroscopy, is about 322 ps,[2] which is only slightly larger than the value calculated by Gil and Kavokin for QDs. The latter makes unclear the conclusion about the giant exciton-light coupling in QDs as compared to bulk ZnO.

An examination of the derivation in Ref. 1 reveals an error, which seemed to affect the final result. First, the properly normalized exciton wave function (w.f.) should read

$$\Phi(\mathbf{r}) = \frac{1}{\sqrt{\pi a_B^3}} \frac{1}{\langle r\rangle^{3/2}} \left(\frac{2}{\pi}\right)^{3/4} \exp\left(-\frac{r^2}{\langle r\rangle^2}\right), \tag{1}$$

which is a factor of 4 less than the one given in Eqs. (4) and (5) of Ref. 1. Second, the integration of Eq. (5) (even with authors' original w.f.) leads to a different result than that given by Eq. (6) of Ref. 1. The correct recombination rate calculated with a properly normalized w.f. is

$$\Gamma_0^{\mathrm{QD}} = \frac{\sqrt{2\pi}}{3} \omega_{\mathrm{LT}} \left(\frac{2\pi}{\lambda_0}\right)^3 \langle r\rangle^3 \exp\left(-2\varepsilon_b \frac{\pi^2 \langle r\rangle^2}{\lambda_0^2}\right). \tag{2}$$

As a result, the maximum $\Gamma_0^{\mathrm{QD}} = \sqrt{6\pi}\omega_{\mathrm{LT}}/(e\varepsilon_b)^{3/2}$ of the recombination rate (2) is reached for $\langle r\rangle = \sqrt{3}\lambda_0/2\pi\sqrt{\varepsilon_b}$. These values are 32 and 2 times larger than those obtained in Ref. 1, respectively. Third, $\langle r\rangle$ in Eq. (1) is not the QD radius, which is implied in Ref. 1, when a conclusion about the dot size of "some 30 nm" is made. To demonstrate this, let us consider the exciton w.f. written as

$$\Phi(\mathbf{r}) = \sin(\pi r/R)/\pi r\sqrt{2Ra_B^3}. \tag{3}$$

Note, that this function is chosen to be exactly zero at $r=R$. Applying to Eq. (3) the same procedure as to Eq. (1), the maximum recombination rate $\Gamma_0^{\mathrm{QD}} = \pi\omega_{\mathrm{LT}}/3\varepsilon_b^{3/2}$ is found for $R = \lambda_0/2\sqrt{\varepsilon_b}$. The latter, as can be expected, indicates that the exciton-light coupling reaches a maximum when the QD diameter is approximately equal the wavelength of light in the QD material. This observation is in line with the calculations of Takagahara[3] for other material systems. Since both exciton w.f. (1) and (3) give almost the same maximum of the recombination rate, one can deduce that $\langle r\rangle = \sqrt{3}R/\pi$. Thus, the minimum $\tau_r$ should have been 264 ps/32=8.2 ps for the QD radius of 16.7 nm$\times 2\times\pi/\sqrt{3}$=60 nm.[4]

In addition, there are two other points that have to be mentioned. First, Eq. (2) gives $\tau_r$=26 000 ps for a ZnO QD with diameter 5 nm. This value is about three orders of magnitude larger than theoretical[5] and experimental[6] estimates for the same QD size. Such overestimation of $\tau_r$ is probably related to the fact that the enhancement of LT-splitting in QDs[7] has not been taken into account. Second, Eq. (2) gives monotonic increase of the recombination rate for QDs with sizes up to 120 nm. However, there are experimental indications that the homogeneous broadening of exciton peaks and the population of lowest excitonic levels at nonzero temperatures lead to a decrease of the recombination rate for QDs with sizes much smaller than 120 nm.[3]

Finally, we feel it is important for experimental data interpretation to plot a corrected size dependence of the radiative lifetime in ZnO QDs. Using the model, which takes into account the valence band degeneracy and anisotropy of wurtzite ZnO QDs as well as the dead-layer effect, we have calculated[5] the exciton radiative lifetime $\tau_1(R)$ for small ZnO QDs (see Fig. 1). For large ZnO QDs, e.g., grains, the radiative lifetime $\tau_2(R)$ has been measured experimentally at 18 K.[8] The combination of these dependencies for two limiting cases shows that the strong decrease of the radiative lifetime is indeed observed in ZnO QDs. At the same time, the minimum of the lifetime and the size of ZnO QDs, at which it is observed, are different from those predicted in Ref. 1. The above minimum of the radiative lifetime shifts

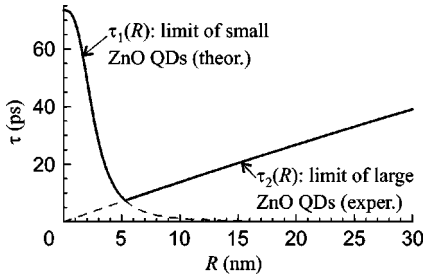


FIG. 1. Radiative lifetime of excitons in ZnO QDs as a function of the OD radius: $\tau_1(R)$ is after Ref. 5 and $\tau_2(R)$ is after Ref. 8 ($T$=18 K).

[a]Author to whom correspondence should be addressed; electronic mail: vladimir@ee.ucr.edu

 

to larger QD sizes and larger lifetimes with increasing temperature.

[1]B. Gil and A. V. Kavokin, Appl. Phys. Lett. **81**, 748 (2002).
[2]D. C. Reynolds, D. C. Look, B. Jogai, J. E. Hoelscher, R. E. Sherriff, M. T. Harris, and M. J. Callahan, J. Appl. Phys. **88**, 2152 (2000).
[3]T. Takagahara, Phys. Rev. B **47**, 16639 (1993).
[4]Note that Gil and Kavokin corrected Eq. (1) in the conference proceeding [Mater. Res. Soc. Symp. Proc. **737**, E13.10 (2003)]. At the same time, instead of the coefficient 2 in the exponent of Eq. (2), they used 8, which led to an erroneous value of $\tau_r$ again. The QD radius (16.7 nm) has not been corrected in the proceeding.
[5]V. A. Fonoberov and A. A. Balandin, Phys. Rev. B **70**, 195410 (2004).
[6]D. W. Bahnemann, C. Kormann, and M. R. Hoffmann, J. Phys. Chem. **91**, 3789 (1987).
[7]M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros, and M. Rosen, Phys. Rev. Lett. **75**, 3728 (1995).
[8]T. Matsumoto, H. Kato, K. Miyamoto, M. Sano, and E. A. Zhukov, Appl. Phys. Lett. **81**, 1231 (2002).