

# Energy relaxation and decay of DX excitons in ZnO nanoparticles excited by VUV photons

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The radiation time of the luminescence of ZnO excitons is faster than typical radiation lifetimes for the same wavelength for most emission centers and excitons in other crystals. Free exciton radiation lifetime is less than 1 ns at ambient temperature, and the radiation lifetime for bounded exciton is about 100 ps at 10K. The most common reasons of the decrease of the radiation time in wide-band-gap insulators under dense or VUV excitation are the dipole-dipole energy transfers to the surface states or to the closely spaced electronic excitations. In ZnO the decrease of the bounded exciton radiation time with the decrease of temperature is accompanied with the increase of the luminescence intensity of this exciton. The phenomenon cannot be attributed only to quenching processes. Many authors refer to a model of the Giant Oscillator Strength [1].

Luminescence decay curves were measured at SUPERLUMI beam station. The intrinsic time resolution of MCP detector was better than 50 ps. In our experiment the measured FWHM of bunch was about 180 ps. We chose a well-known decay function for luminescence intensity with account for the dipole-dipole energy transfer:  $I(t) \sim \exp(-t/\tau - q(t/\tau)^{0.5})$  as a model function for the fitting of experimental decay curves. In this function the first exponential term is the monoexponential decay with the radiation lifetime  $\tau$ , the second term, containing the square root of time, is the “quenching” term and  $q$  is the parameter characterizing the degree of deviation from exponential law. The decay during the non-exponential initial stage can be also characterized by “instantaneous” decay time:  $\tau_i(t) = -1/(d \ln I(t)/dt)$  calculated based on the fitting curves.

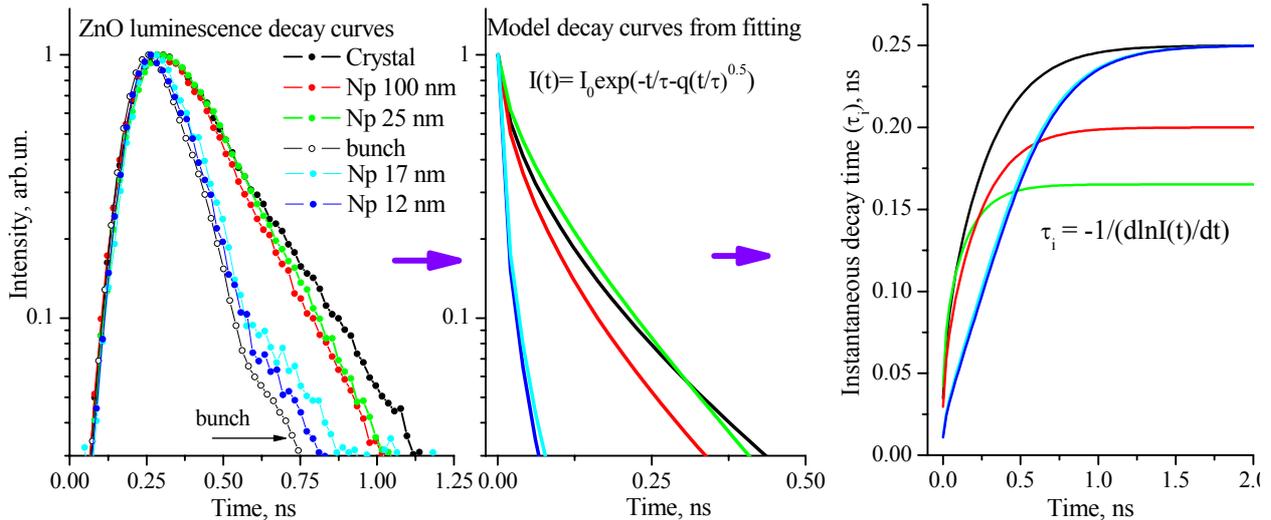


Figure 1: Left panel: decay curves measured for monocrystal and nanoparticles at temperature 8K and excitation at 4eV (colors of points and lines: black – monocrystal, red – 100 nm nanoparticles, green – 25 nm nanoparticles, cyan – 17 nm nanoparticles, blue – 12 nm nanoparticles, open points - instrument response curve, bunch). Middle panel: model decay curves calculated using the fitting procedure. Right panel: instantaneous decay time.

Figure 1 demonstrates the dependence of DX (i.e. exciton bounded at the donor) luminescence decay on the size of ZnO nanoparticles [2] and monocrystal excited by 4 eV photons. We can distinguish three ranges of sample sizes. The first size range is formed by relatively big particles with diameter from 100 nm up to infinity (monocrystal). Samples from this range shows the decay time ( $\tau$ ) of about 250-300 ps and the quenching is small ( $q \sim 0.2-0.4$ ). The second range includes the particles of intermediate size between 20 and 100 nm. ZnO particles from this range demonstrate very strange properties: high luminescence intensity without quenching ( $q \sim 0.1-0.2$ ), and show practically exponential decay with very fast characteristic decay time (about 150 ps). The third range corresponds to small nanoparticles with diameter less than 20 nm. The experimental decay curves are very close to the bunch profile. Luminescence is strongly quenched for these particles ( $q \sim 2-5$ ), the typical luminescence decay kinetics demonstrates significant deviation from the single exponential law, the estimated radiative decay time is 250 ps. At 4 eV excitation each photon creates in ZnO one electron-hole pair with energy close to the forbidden energy gap. Therefore, the probability of direct formation of DX exciton is high. Assuming that the intensity of synchrotron radiation at the sample surface is low, we suppose that the distance between excitons is much larger than the characteristic length of dipole-dipole interaction. Therefore the excitons cannot be quenched due to the exciton-exciton dipole-dipole interaction, and we suppose that the main reason of the quenching should be the energy transfer to surface states.

The modification of decay kinetics can be expressed as variation of relative luminescence yield. This parameter characterizes the contribution of quenching process in luminescence decay. Figure 2 shows the variation of relative yield with the increase of the excitation photon energy up to 30 eV.

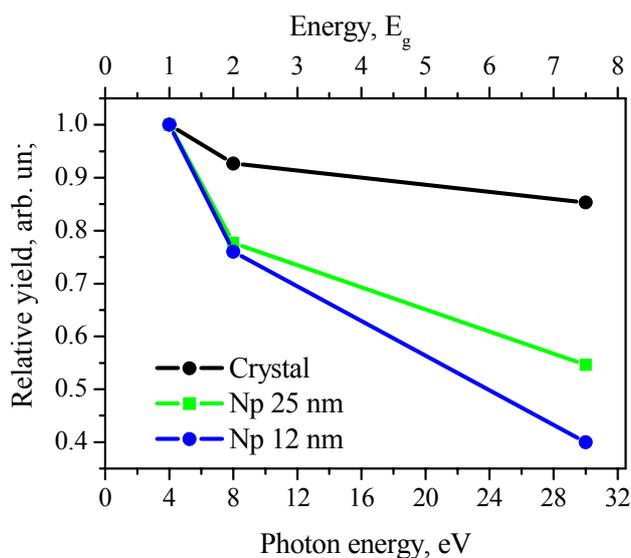


Figure 2: Variation of relative luminescence yield with excitation energy increase (yield at 4 eV excitation is 1) for monocrystal (black line), 25 nm nanoparticles (green) and 12 nm nanoparticles (blue).

The acceleration of the decay with excitation energy is observed in all samples. The effect must be similar to the luminescence quenching observed in many crystals when the excitation energy exceeds the first threshold of multiplication of electronic excitations ( $\sim 2E_g$ ). The creation of two and more electronic excitation on the distance of interaction is responsible for this quenching. For the first time we observe the amplification of this effect with the decrease of the particle size. This new phenomenon can be connected with the modification of the distribution of electronic excitation in nanoparticles at thermalization stage.

## References

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- [2] D. Tainoff, B. Masenelli, O. Boisron, G. Guiraud and P. Mélinon, *J. Phys. Chem. C*, 2008, 112 (33), 12623–12627.