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Temperature and size dependence of time-resolved exciton recombination in ZnO quantum dots

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ZnO nanocrystals with various sizes were prepared and characterized. Their photoluminescence dynamics has been investigated at low temperatures. For the smallest particles (3 nm), a defect-induced long-lived photoluminescence occurs around 2.5 eV which is slowed down at decay times longer than 3 ns when sample temperature T decreases. From thermal quenching of the 2.5 eV band, the exciton dissociation energy at defect centers is estimated around ~11.8 meV. For larger crystallites (10 and 20 nm), the ultraviolet emission observed at 3.32 eV decays in less than 85 ps and follows a Varshni law [Y. P. Varshni, Physica (Amsterdam) 34, 149 (1967)]. © 2011 American Institute of Physics. [doi:10.1063/1.3669511]

ZnO is a wide bandgap n-type semiconductor suitable for devices and ultraviolet (UV) lasers,¹–³ which exhibits two strong photoluminescence (PL) massifs in the UV and visible range at room temperature (RT).⁴ The first UV emission at 3.30 eV (375 nm) is usually ascribed to the main contribution of near-band-edge (NBE) free excitons. The broader ZnO emission of the green spectral range (hereafter referred to as G band) occurs between 2.2–2.5 eV (480–560 nm) and reflects various types of intrinsic defects always present in the ZnO structure, especially occurring in quantum dots (QDs) and nanocrystals.⁵

While absorption and fluorescence studies of ZnO QDs are well documented, there are fewer reports⁶,⁷ on the combined influence of sample temperature, size, and intrinsic defects on the quantum confinement effect and the exciton decay dynamics of both NBE and G bands in ZnO nanostructures. In this letter, we study these properties on as-synthesized pristine ZnO nanocrystals with different controlled sizes (3–20 nm) produced by soft chemistry routes.⁸,⁹ Transmission electron microscopy (TEM) images and x-ray diffraction Rietveld refinements show that our ZnO nanoparticles have a characteristic hexagonal shape with the wurtzite structure type.

We expect that our smallest nanoparticles of size 3 nm with a radius smaller than the bulk ZnO Bohr radius (a_B = 2.34 nm) (Ref. 10) can have relatively high exciton energy, and that charge carriers are in strong confinement regime. Exciton energy in quantum dots with radius larger than the ZnO Bohr radius is relatively smaller in comparison, and carriers in these dots are in the weak quantum confinement regime. Thus, in the present work, our ZnO nanoparticles of size 5 nm and size 10–20 nm should lie in the intermediate and weak confinement regimes, respectively.

Fig. 1(a) shows that the optical absorption edge depicting the energy of the lowest excited state of the exciton shifts towards high energies as the size of our particles decreases. This trend can be reproduced by expressing the energy of the lowest excited state as a function of the nanocrystal radius R,¹¹

\[ E(R) = E_x + \frac{\hbar^2 \pi^2}{2 R^2 \mu} \frac{1.786 e^2}{4 \pi \epsilon_0 \epsilon R} \]

where \( \epsilon_0 \) and \( \epsilon \) are the permittivities of free space and particles, \( e \) the elementary charge, and \( \mu \) the reduced effective mass of the electron \( (m_e^* \) ) and the hole \( (m_h^* \) ). The best fit with Eq. (1) to the experimental absorption mid-edges energies is obtained for \( m_e^* = 0.24 \), \( m_h^* = 0.45 \), and \( \epsilon = 3.7 \) in good agreement with an intermediate confinement regime.

![Fig. 1](image-url)
characterized by $m^*_e < m^*_h$. This curve yields averaged particle sizes in solution of 4, 6, 7, and 14 nm. It is seen that $E$ is almost saturated while extending to the upper size limit. The particles were studied additionally using steady-state PL with resonant excitation at 325 nm (3.81 eV). A strong UV peak is observed, progressively red-shifted as size increases (Fig. 1(a), lower curve), and located at 3.406, 3.342, 3.263, and 3.179 eV for 3, 5, 10, and 20 nm diameters, respectively. This PL band has been resolved into several constituent bands stemming from acceptor-bound AX excitons, donor-bound DX excitons (at 3.25 eV), and free X excitons. Bands stemming from acceptor-bound AX excitons, donor- and 3.179 eV for 3, 5, 10, and 20 nm diameters, respectively. This PL band has been resolved into several constituent bands stemming from acceptor-bound AX excitons, donor-bound DX excitons (at 3.25 eV), and free X excitons.

Confinement effect is confirmed by a Stokes-shift increase of about 100 meV from 20-nm to 3-nm size.12,14,15 The confinement effect is confirmed by a Stokes-shift increase of about 100 meV from 20-nm to 3-nm size.12,14,15 The particles were studied additionally using steady-state PL experiments using a femtosecond laser and a streak camera system as in our previous studies.16,17 Fig. 1(b) shows the room-temperature transient PL spectra, integrated over a time of 1 ns, for the different sizes. All nanoparticles show two distinct transient emission bands, the UV peak matching well the resonantly excited ZnO near-band-edge steady-state emission around 3.10–3.35 eV with a minor unresolved band around 2.98 eV, and a broad emission G-band in the blue-green region of the spectrum which is attributed, like for the steady-state PL case, to intrinsic point defects.18 There is also a blue shift of the transient UV peak from 3.10 to 3.35 eV ($\Delta E = 0.25$ eV) with size reduction. Results of Figs. 1(a) and 1(b) can be naturally explained by the quantum confinement, which shifts the energy levels of the conduction and valence bands apart, causing a blue shift in the transition energy as the size of nanoparticles decreases.

An intriguing result here is that the relative intensity of the two transient PL bands depends on the size of the nanoparticles. The inset of Fig. 1(b) shows that the defect-related transient band peaked around 2.5 eV (G band) is strongly enhanced with size reduction, i.e., with the increase of the total surface area in the particle ensemble volume resulting from the larger surface area to volume ratio.19 Between the two extreme sizes, this intensity enhancement is roughly of a factor of 10. Additionally, we observe that the emission of the defect-induced G band is longer-lived as the size of nanoparticles decreases at RT (Fig. 2(a), inset). These data suggest that several trap states originating from surface defects are involved in the radiative recombination occurring around 2.5 eV in smaller particles. The luminescent species trapped at surface defects survive longer before recombination without being perturbed by their environment. In this case, the luminescence decay is longer-lived. From the energy difference at stake ($>3k_BT$), we may ascribe the 2.5 eV emission (2.6 eV at 10 K) to a transition involving nonbonding donor oxygen-vacancy levels formed from sp$^3$ hybrid orbitals and located in the gap.5,20

Temperature dependent experiments down to $T = 8–15$ K were carried out for all samples. For the smaller 3-nm QDs (Fig. 2(a)), we record the strong defect band around 2.57 eV with a small low energy component at 2.17 eV. The PL kinetics (Fig. 2(b)) are reproduced by a Kohlrausch-Williams-Watts law,21

$$n(t) = n_0\exp[-(t/\tau)^\beta].$$

Here, $n_0$ is the excitation population $n(t=0)$ and $\tau$ the characteristic Kohlrausch time. The stretching exponent ($0 < \beta \leq 1$) can expressed by $\beta_k = D/(D + 2)$, where $D$ is the effective dimensionality of the configuration space in which the excitons relax.22 The average lifetime of this distribution is $\langle \tau \rangle = \tau_k\Gamma(\beta_k^{-1})$, where $\Gamma$ is the Gamma function. Assignment of Eq. (2) to experimental decays of ZnO nanocrystals is justified in the case of ensembles in which particles are not isolated from each other. The average decay time of the 3-nm QD defect emission is strongly $T$-dependent raising from 1888 ps at RT to 3194 ps at 10 K with drastic increase below 150 K. Concomitantly, the dimensional parameter $\beta_k$ decreases from 0.69 at RT to 0.58 at 10 K; i.e., the PL relaxation is more dispersive with more spread relaxation rates. In this case, there is slower 3D relaxation in the presence of short range forces. We measure a small upshift in energy of 30 meV between ambient temperature and 10 K.

The thermal quenching of the G band can be directly obtained from the decay curves of Fig. 2(b). The plot of the PL intensity 4 ns after excitation vs. $1/T$ can be reproduced by an Arrhenius model,23

$$I_{PL}(T) = I_0[1 + c_1\exp(-E_1/k_BT) + c_2\exp(-E_2/k_BT)]^{-1},$$

FIG. 2. (Color online) Temperature dependence of the transient PL for 3-nm ZnO nanoparticles from RT to 10 K. Time-resolved emission spectra (a). In inset, the decays of the G band for the two extreme sizes 3 nm ($\tau = 1.88$ ns, $\beta_k = 0.69$) and 20 nm ($\tau = 309$ ps, $\beta_k = 0.71$) are compared at RT. PL kinetics of 3 nm nanocrystals (b) with signals spectrally integrated between 1.96 eV and 3.87 eV. Inset: Variation of the average Kohlrausch lifetime and stretching exponent from fits to the decays. Thermally activated PL quenching of the G band at $t = 4$ ns after excitation (c); $\lambda_{ex} = 267$ nm.
The two major emissions related to confined excitons in the UV region and to defects in the green spectral range. The former ultrashort-lived UV band shifts to higher energy when QD size is augmented. This emission follows a Varshni law at low temperatures showing that it originates mainly from free excitons. The latter PL band tentatively ascribed to oxygen vacancies at dot surfaces shows long-lived decays with exciton dissociation energy of about 11.8 meV.

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In this work, we define the Stokes shift as the energy difference between the absorption maximum (different from the absorption edge energy) and the maximum of the steady-state photoluminescence peak in the UV region.
Y. P. Varshni, Physica (Amsterdam) 34, 149 (1967).