Photoluminescence and structure study in mixture of ZnO and carbon nanoparticles during mechanical activation

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Abstract. The photoluminescence and X ray diffraction of the mixture of ZnO + 1.0% C nanocrystals (NCs) have been studied before and after intensive mechanical processing (MP) with the aim to identify the nature of emission bands and radiative defects. The study reflects the diversity of physical processes occurring during MP: the destruction of primary ZnO NC aggregates, crushing individual ZnO NCs from the size of 250 nm down to 14 nm, the interaction of carbon atoms with oxygen in a treatment chamber and with the surface of ZnO nanoparticles etc. The new PL band peaked at 2.84-2.95 eV has been revealed in PL spectra after 9 min of MP. The origin of this emission in ZnO has not been conclusively established. The new PL band peaked at 2.84-2.95 eV has been studded and its nature is discussed.

1. Introduction
ZnO nanocrystals (NCs) with the native defects or different type dopants are the one of most popular new systems (1). ZnO NCs with a direct band gap (3.37 eV) and a high exciton binding energy (60 meV) at 300K promise numerous applications in optical and electronic devices (1, 2), such as: catalytic materials (3), solar cells (4), field emission cathodes (5, 6), luminescent materials (7) etc. Important electronic properties have been revealed in the nanocrystalline composites ZnO + xC recently, which permit improving the field emission properties of cathodes (5), engineering room-temperature ferromagnetism (8), modify luminescence properties (9), and to create the selective solar absorbed coatings (10). The creation of efficient electronic devices requires to study the emission nature and the mechanisms of defect generation in ZnO NCs. In present paper the transformation of photoluminescence (PL) and its temperature dependences have been investigated for the mixture of ZnO + 1.0% C NCs with the goal to study the nature of PL bands, the PL quenching mechanism, the radiative defect nature and the process of defect creation at mechanical processing (MP).

2. Experimental details
ZnO NCs (99.5 % purity, Reasol; with the particle size of dZnO ~ 250 nm) and carbon nanoparticles (EPRUI Nanoparticles & Microspheres Co. Ltd.) were mixed. High resolution TEM images (performed earlier) have shown that the carbon nanoparticles are characterized by a spherical-like shape with an average diameter of dC ~ 50 nm. Mechanical processing (MP) of ZnO + xC mixtures with x = 1.0 % wt. was carried out in a Planetary Ball-Mill (PM 400/2, Retsch Inc.). The grinding chamber of 50 ml with the tungsten carbide balls (3 of 20 mm and 10 of 10 mm) were used. The weight ratio of balls to mixture powder equal to 28:1 has been used. MP was carried out with the rotation speed 400 rev/min for processing times (tMP) of: 1, 3, 9, 30, 90 and 390 min. The early X ray diffraction study has shown that the average ZnO NC sizes, estimated using Sherrer formula (11), decreases from 250 nm in an initial state down to 14 nm for tMP = 390 min.
PL spectra were measured at 300K and the excitation by a He-Cd laser with a wavelength of 325 nm and a beam power of 46 mW using a PL setup on a base of spectrometer SPEX500 described in (12,13) in the temperature range of 10-300K.

3. Experimental results and discussion

PL spectra of the ZnO + 1% C mixture at 300 K measured for the different MP times are shown in figure 1.

![Figure 1. PL spectra of ZnO+1% C NCs at different moments of MP: (a) 1-1min, 2-3min, (b) 1-3min, 2-9min, 3-90min, 4-390min](image)

It is clear that PL spectra are complex and can be represented as a set of PL bands. The PL spectrum measured after 1 min of MP can be decomposed on three PL bands with the peaks at: 3.14 eV (I), 2.42-2.50 eV (II) and 1.57 eV (III) (Fig. 1a, curve 1). The UV and visible PL bands in ZnO NCs are attributed to the near-band-edge (NBE) (I) and defect related (II) emissions (14-18).

NBE emission in ZnO NCs, as a rule, is related to the free or defect bound excitons with their phonon replicas, and/or the donor-acceptor pairs (14,15). It was shown earlier in (16,17) that free exciton emission or its replicas dominate in ZnO NC spectra at room temperature owing to the high free exciton binding energy (60 meV) at 300K and the fast decay of the PL intensities of bound exciton and donor-acceptor pair emissions with increasing temperature in the range of 10-300K. Thus the high PL intensity and a small half width of 3.14 eV PL band in PL spectra of the ZnO + 1% C mixture at 300K permit assigning NBE emission to the LO phonon replicas of free exciton emission in ZnO NCs. The nature of IR PL band peaked at 1.57 eV (III) is not clear. Note that in our experiments (presented below) this PL band intensity varies by the same way as the PL intensity of 3.14 eV PL band. Thus we can attribute the IR PL band at 1.57 eV (III) to the second order diffraction peak of the 3.14 eV PL band (15-18).

The PL intensity mentioned above PL bands decreases dramatically at MP and the new PL bands with peaks at 2.84 -2.95 eV, 2.10-2.20 eV and 1.42-1.47 eV have appeared (Fig. 1b). The variation
kinetics of the integrated PL intensities for all PL bands at MP are presented in figure 2. As it is clear there are two stages in this kinetics depending on the duration of MP process.

**First stage.** The PL intensity decreases upon the first MP stage (1-9 min) with nearly the same rates for the NBE and defect related PL bands. This effect can be assigned to the generation of nonradiative recombination centers (NR) at MP. The PL intensity is proportional to the quantum efficiency ($\eta$) of visible recombination (19). The increase of NR center concentrations stimulates the rise of NR recombination rate together with falling down the PL intensity at MP. Linear dependences of the PL intensity decay for the stage I, presented in logarithmic scales (Fig. 2), testify on the hyperbolic PL intensity variation versus time. Note that NR centers can be assigned to the dangling bonds on the surface of ZnO NCs created at crushing the individual ZnO nanoparticles at MP. Simultaneously, in the first MP stage the peak of defect related PL band (II) shifts to 2.11-2.25 eV and the new PL bands peaked at 2.84-2.95 eV and 1.42-1.47 eV appear (Figures 1b).

**Second stage.** The new PL bands with the peaks at 2.11-2.25 eV, 2.84-2.95 eV and 1.42-1.47 eV dominate in the PL spectra of all samples after 9 min of MP (Figures 1b). The defects, responsible for the 2.11-2.25 eV PL band, can exist in the original ZnO NCs or their concentration can increase at MP as well. The IR PL band peaked at 1.42-1.47 eV is attributed to the second order diffraction peak of 2.84-2.95 eV PL band. The high energy PL band is characterized by the peak at 2.84-2.95 eV in the different samples of ZnO+1%C NC mixture.

In order to gain more insight on the light-emitting mechanism of the ZnO+1%C NC mixture and to recognize the different types of optical transitions, we have performed the temperature dependent PL measurements in the range of 20-300K (Fig. 3).
The deconvolution procedure has been applied to all PL spectra measured at different temperatures from the range 20-300K to gain the detailed analysis of their temperature behavior. The five PL bands have been used at 300K for the deconvolution process: 3.14, 2.92, 2.58, 2.23 and 1.46 eV (Fig.4a). The change of PL peak positions for the mentioned PL bands at the temperature variation is presented in figure 4b. As one can see from Fig.4b, the PL band (2) peaked at 2.92 eV does not change its PL peak position with temperature. In contrary the other PL bands (1-3.14eV, 3-2.58eV and 4-2.23eV at 300K) monotonically shift to higher energy at the temperature decreasing. The last behavior is typical for the PL bands in the ZnO NCs and related to shrinking the energy band gap at higher temperatures (17). Note that the analysis of the PL peak shift versus temperature (Fig.4b) has been done using the well-known Varshni formula $E(T) = E_0 - aT^2/(T+b)$ (20), where $E_0$ is the band gap at the absolute temperature $T = 0$ K; “$a$” and “$b$” are the Varshni thermal coefficients. The fitting parameters “$a$” and “$b$” were estimated in studied samples as $a = 0.975$ meV/K and $b = 750$K. These values are very close to fitting parameters estimated earlier for the band gap shrinkage in the bulk ZnO ($\alpha$ equal 0.981meV/K and $\beta$ equal to 650K) (21). Thus we can conclude that the PL bands peaked at 3.14, 2.58 and 2.23 at 300K related to emission in ZnO NCs. The nature of the 2.92eV PL band needs to be discussed additionally.

![Figure 3](image1.png)

**Figure 3.** PL spectra of studied ZnO+1% C NCs measured at different temperatures after MP for 390 min

![Figure 4](image2.png)

**Figure 4.** Deconvolution procedure applied to the PL spectrum measured at 300K of the ZnO+1% C NCs after MP for 390min (a), and (b) The variation of PL peak positions versus temperature for the PL bands 1,2,3 and 4
A variety of emission bands in UV and visible spectral ranges have been detected in ZnO NCs earlier (14,18). The origin of these emissions has not been conclusively established. The blue PL band with the peak at 2.80-2.90 eV in ZnO is attributed earlier to Cu related defects in (21,22), to Zn interstitials (23) or to the donor–acceptor pairs included the shallow donor and oxygen vacancy (24). In our case we can attribute the 2.92 eV PL band to emission of the graphene or graphite oxides covered the surface of ZnO NCs (25-27). Note that the PL spectra of carbon quantum dots were detected earlier in the spectral range 2.75-2.95eV as well (28).

The PL spectra of graphene and graphite oxides [25], as well as of the studied ZnO+1%C NC mixture after MP are presented in figure 5 for the comparison. The corresponding PL peak positions are: 2.79 eV in the graphite oxide, 2.95eV in the graphene oxide and 2.92 eV in the studied mixture. Thus the new high energy PL band in our samples is characterized by the intermedium position between the positions of luminescence bands typical for the graphite (graphene) oxides. Note that the graphite (graphene) oxides can be created at the oxidation of carbon nanoparticles at prolonged MP. To make the final conclusion concerning the nature of 2.84-2.95 eV PL bands the additional deep study is necessary.

4. Conclusion
The transformations of PL spectra and XRD diagrams in the ZnO NCs + 1%C mixture at mechanical processing have been investigated. Two stages of PL spectrum transformation have been revealed and discussed. It is shown that the first stage is connected with the quenching of PL intensities of all PL bands owing to the nonradiative center appearing at crushing the individual ZnO NCs and decreasing their sizes from 250 nm down to 14nm. The second stage of PL spectrum transformation at MP is connected with appearing the new 2.84-2.95 eV and 2.11-2.25 eV PL bands. The former one is attributed to emission in the graphite (graphene) oxides.
5. References

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