JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 2, February 2008, p. 288 - 293

Photoluminescence properties of composites based on zinc oxyde and single-walled carbon nanotubes

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Photoluminescence (PL) properties of the composites based on zinc oxide (ZnO) and single-walled carbon nanotubes (SWNTs) prepared by hydrothermal synthesis are studied in this paper. The emission and excitation spectra of nanometric ZnO powder are dramatically influenced by the adsorption of different molecules coming from the environment. Therefore, a special attention is given to reveal the influences of adsorption/de-sorption process on photoluminescence properties of zinc oxide nanoparticles. A quenching effect of the intrinsic PL is observed regularly when the ZnO is synthesized in the presence of SWNTs, i.e. when a ZnO/SWNTs composite is formed. A distinct feature of the ZnO/SWNTs composite, is an emission band with a maximum at 405-450 nm.

(Received September 25, 2007; accepted February 7, 2008)

Keywords: Photoluminescence, Properties and materials, Composite materials, Nanocrystalline materials, Nanotubes

1. Introduction

Zinc oxide (ZnO) is a promising material for a variety of practical applications as UV-light emitters, chemical and gas sensors, optical waveguides, surface acoustics wave devices, transparent conductive oxides, etc. [1]. Therefore, a considerable interest in the studies of ZnO as powder, single crystals, thin films or nanoparticles has recently emerged. ZnO is a direct gap semiconductor whose room temperature PL is of the greatest importance. Different ZnO nanostructured morphologies (nanowires, nanorods, tetrapods, nonoribons/belts, nanorings, nanohelixes, nanosheets, hierarchical nanostructures, etc.) have been associated with some peculiarities of PL spectra excited with light of energy matching the fundamental absorbtion band.[2] Depending on the nanoparticle morphology, different band edge of ZnO nanostructures was reported: 373, 378, 380, 383, 387 and 390 nm [2]. One possible reason for the variations in the position of the band-edge emission in various ZnO nanostructures is the different concentration of native defects. In nanostructures of different sizes, the intensity and composition of the PL spectra strongly depend on the surface-to-volume defects ratio [3]. In the most cases, the PL of ZnO nanostructures is characterized by a weak UV edge emission and a strong wide band in which one find many components, located in the visible range of the optical spectrum, closely related to the nanostructure surface defects [4-6]. Therefore, clarifying the origin of different defect emission bands is an important issue. More precisely, for different ZnO nanostructures, emission bands localized in the spectral ranges 405-446, 466-583 and 640-680 nm, for short violet-blue, green – orange and red bands, respectively have been reported [2]. Despite these numerous studies concerning the growth and properties of ZnO nanostructures, there are still a number of unanswered questions concerning the relationship between fabrication conditions and optical properties [2]. A recently developed topics concerns the preparation of composites based on carbon nanotubes (CNs) and ZnO [7-12]. The interest for these composites has been generated by possible applications as field emission sources and materials with higher photocatalytic activity [7,8]. Although CNs were coated with various ZnO structures such as ribbon, comb, nanowires and ZnO thin films, further studies concerning techniques and synthesis methods are still required in order to find additional applications for these nanocomposites. The studies and the interest for the ZnO/SWNTs composite are still at an initial stage and many questions await an answer. Two mechanisms have been proposed for the attachment of ZnO nanoparticles to CNs: non-covalent functionalization [8] and electrostatic coordination [9].

This work present new data of photoluminescence on ZnO/SWNTs composites prepared by hydrothermal-chemical synthesis. A special attention is given to variation of the luminescence spectra of ZnO and ZnO/SWNTs nano-powder with the experimental measuring conditions.

2. Experimental

In this work we use two ZnO samples: one purchased from ALDRICH and another prepared by hydrothermal route. The latter samples, ZnO and ZnO/SWNTs composites, in form of powder were obtained by hydrothermal synthesis using 0.001 mol $ZnCl_2$ and 0.002 mol KOH dissolved into small amount of distilled water, about 10 ml. A good dispersion of SWNTs was obtained by one hour ultrasonic treatment of carbon nanotubes pluged in a KOH solution. Mixing the two solutions, i.e. $ZnCl_2$ and KOH+SWNTs, a grey solution immediately appears. The grey color is due to the ZnO/SWNTs agglomerated cake formed in the reacting solution. After adding of 5×10^{-3} mol cetyltrimethylammonium bromide (CTAB) under stirring, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave of 40 ml and filled by distilled water up to 80% volume. Hydrothermal treatments were carried out at 120 °C for 5 hours. After that, the autoclave was cooled naturally and a grey precipitate was collected and washed with distilled water and ethanol several times to remove impurities. Afterwards, the precipitate was dried at 50 °C for 5 hours.

PL and PL excitation spectra were measured on powder of ZnO and ZnO/SWNTs in a right angle geometry using a Jobin Yvon Fluorolog-3 spectrometer, model FL3-22 under identical excitation conditions.

3. Results and discussion

As for any nanometric powder, the intensity and the features of the PL spectra of ZnO nanoparticles strongly depend on the adsorption processes. The oxygen plays an important role. The surface-to-volume defects ratio becomes an important parameter in defining the nature of luminescence process for such materials. The role of the surface as localizing both the structural crystalline lattice defects and adsorbing sites for the foreign molecules come from environment can be revealed by variations of the PL spectra with temperature, working pressure and nature of the ambient gas. A priori, the main luminescence of the zinc oxide, which is a direct gap semiconductor, originates in the excitons radiative recombination. Such a process is strongly dependent on the nature and the density of the recombination defects. Defects such as vacancies, excess of oxygen atoms, impurities are localized both in the bulk or at the surface of the particle. In the former case, the PL has the bulk signature, which is similar with that is observed on a macroscopic sample, for example a single crystal. In the latter case, due to the adsorption process, the PL emission strongly depends on the environmental conditions, sometimes intense enough to hide the bulk emission. This explains to a large extent both the great dispersion of reported PL data on different nanometric powders as ZnO, SiO_2, TiO_2, etc and their dependence on the experimental measuring conditions. A convincing evidence about the mystification of the PL spectra of nanometric powders by adsorption effect is offered by the variation of the luminescence intensity of spectral and decay time if the measurements are performed in air, vacuum or after a de-sorption heat treatment at a moderate temperature, for example 150 °C, made in vacuum of 10^{-6} mbar or in air. All these facts, strongly affecting the validity of the reported results, make a difficult task to explain in all details the PL data of a nanometric powders. The greatest part of reported data deals with the variation of the PL spectra of ZnO with the morphological form of particles - nanowires, nanorods, tetrapods, nonoribons/belts, nanorings, nanohelixes, nanosheets, hierarchical nanostructures. No much attention was paid in divulging the role of the experimental measuring conditions, how these may change the PL spectra of ZnO particles. Observing the literature devoted to the PL of ZnO nanometric powder one relieves that no net dependence of the PL emission on measuring experimental conditions has been reported yet. Establishing this frame, the present paper aims evidencing the SWNTs signature in the PL emission of ZnO/SWNTs composites hydrothermally synthesized in different experimental measuring conditions. In this context, we investigated the variation of the PL emission of a hydrothermally prepared ZnO powder at room (RT) and at liquid nitrogen temperature (LNT). The measurements at RT were performed on as prepared samples, in air, in vacuum (10^{-6} mbar) before and after a de-sorption heat treatment at 150 °C and again in air. The measurements at LNT were performed before and after the de-sorption heat treatment at 150 °C vacuum. The Fig. 1a is fully illustrative: it shows a typical variation of the PL emission of nanometric ZnO powder, with particle of 60-80 nm mean size, purchased from ALDRICH, when the experimental measuring conditions are changed. PL spectrum of ZnO nanoparticles measured at room temperature in air under UV excitation, at 335 nm (3.7 nm), contains two main bands at about 3.2 eV of excitonic origin and 2.3 eV ordinarily labeled “the green band”. Analyzing the profile of the latter band, one find three components at about 2.7, 2.15 and 1.82 eV which vary differently changing the experimental measuring conditions. Fig. 1b presents the excitation spectra associated with these three components. As one see, the emission bands 2.15 and 1.82 eV, are properly excited with light of 3.28 eV that coincides with the exciton transition. This fact originates in excitons recombination processes involving surface states. As argument we notice the great decrease of these bands intensity observed when the measurements were performed in vacuum (red curve) or after a desorption heating treatment in vacuum at 150 °C (green curve). In this frame, an irrefutable argument providing the strong dependence of the PL emission of nanometric ZnO powder on the ambient conditions arises from the recovery of the broad green emission band, to its initial intensity, if the measurements are performed again in air (blue curve in Fig. 1a). The oxygen is the most plausible adsorbed gas from the environments. Contrary to the expectations, the oxygen known as quenching agent for a large variety of PL emitters, in the particular case of ZnO, its presence contributes largely to the enhancement of the green band [13].

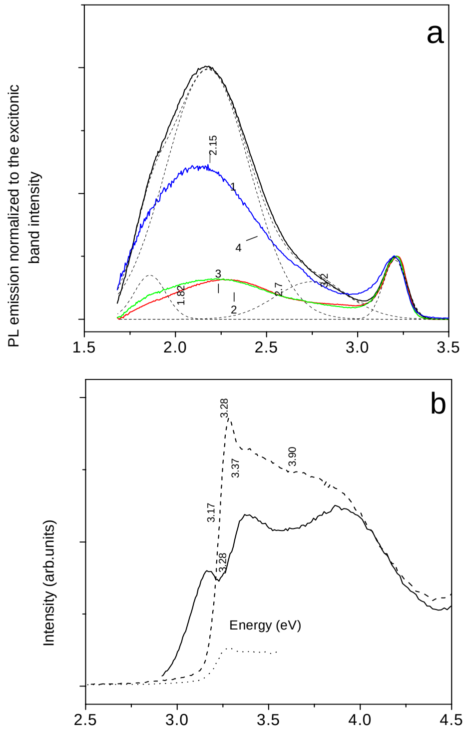

Fig. 1. PL spectra of Aldrich nanometric powder measured at room temperature in air (curve 1), in vacuum (1 10^{-6} mbar; two hours of pumping) (curve 2), in vacuum after 2 hours of heat treatment at 150 ^{0}C in vacuum (curve 3) and again in air (curve 4). Fig. 1b shows the excitation spectra recorded in air for the emission bands at 2.7 eV (solid line), 2.15 eV (dashed line) and 1.82 eV (dotted line) measured in air.

A different excitation spectrum is observed for the emission band peaking solid curve in Fig. 1b. The three maxima, identified at 3.17, 3.37 and 3.9 eV, not more matching the 3.28 eV exciton transition, indicate that in the generation of the ZnO luminescence are involved other PL processes, not strictly related of the nature of the nanoparticle support. A supplementary argument in this sense is offered by the great similarity of the PL emission of different nanometric powder as ZnO, TiO_2, SiO_2 when it is measured in air. Summarizing all above we precise the followings; i) the intensity and spectral distribution of the PL of ZnO nano-powder strongly depend on the excitation wavelength; ii) the emission spectra are sensitive to the experimental measuring conditions; iii) the excitation spectra associated with different PL bands relate not uniquely the optical properties of the ZnO particle. This means that a proper excitation ligh does not coincide with the energy need for a band-to-band or exciton transition. In the light of these, the scheme of luminescent centre associated with a ZnO nanoparticle can be illustrated as in Fig. 2. A nanometric powder may contain particles of different size and shape as rods, platlets, ellipsoids, etc. Such a schema discerns a ZnO core and an interface zone (1) where one find molecules strong attached to the ZnO particle. Another thicker covering (2) contain molecules weakly bound.

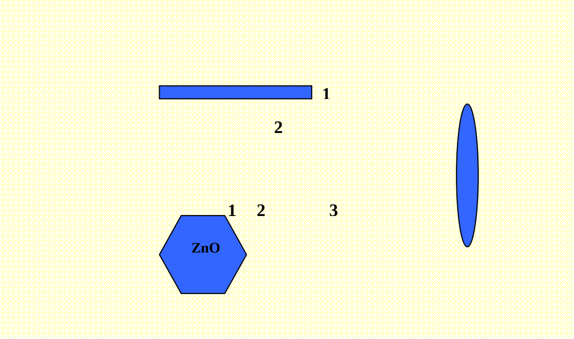

Fig. 2. Schema of a nanometrc powder containing particles of different size and shape. In the interface zone (1) one find molecules strongly attached to the ZnO particle while the zone (2) contains molecules weakly bonded.

These particles plunged in the environment (3) form together the nanometric powder. The environment can be the ambient atmosphere in which one find different gazes or the vacuum. Under an exciting light, different absorption processes occur in the core of the particle when the energy of exciting light matches with the band gap energy of ZnO and in the interface zones 1 and 2 if these contain absorbing molecular species. In general the absorption processes developed in the covering zones occur for light of different energy than that corresponding to the band-to-band transition in ZnO particle. This explains the appearance of different PL spectra whose correspond different excitation spectra.

Using this schema is easy to understand why one obtains different PL spectra of the ZnO powder if the measuring conditions are changed. In this way the PL spectra shown to the Fig. 1 become easily explainable: the band at 2.15 eV, very sensitive to the environment measuring conditions, reveals in the greatest part the signature of the nano-particle clothing formed from adsorbed molecules from environment while the band at 3.2 eV originates in the radiative exciton recombination in the ZnO particle. The excitation spectra presented in Fig. 1b support also this reasoning.

Relating these of the PL emission of ZnO/SWNTs composite we are tempted to consider that the emission band at 2.7 eV is the most convenient in revealing the SWNTs signature [14].

Accounting all these we present hereinafter the PL spectra of a ZnO and ZnO/SWNTs composite prepared by hydrothermal route.

Fig. 3 shows a complex variation of the PL spectra of ZnO nanometric powder with the wavelength of the excitation light and other experimental measuring conditions. The recording cycle of PL in different conditions has begun measuring the PL in air at room temperature (RT) of an as prepared sample (black curve), followed of one in vacuum, after two hours of pumping at

5×10^{-6} mbar (red curve), in vacuum at RT after a thermal treatment of 2 hours at 150 ^{o}C (green curve), again in air at RT (blue curve). Two measurements at liquid nitrogen temperature (LNT) were performed before and after the sample heating at 150 ^{o}C.

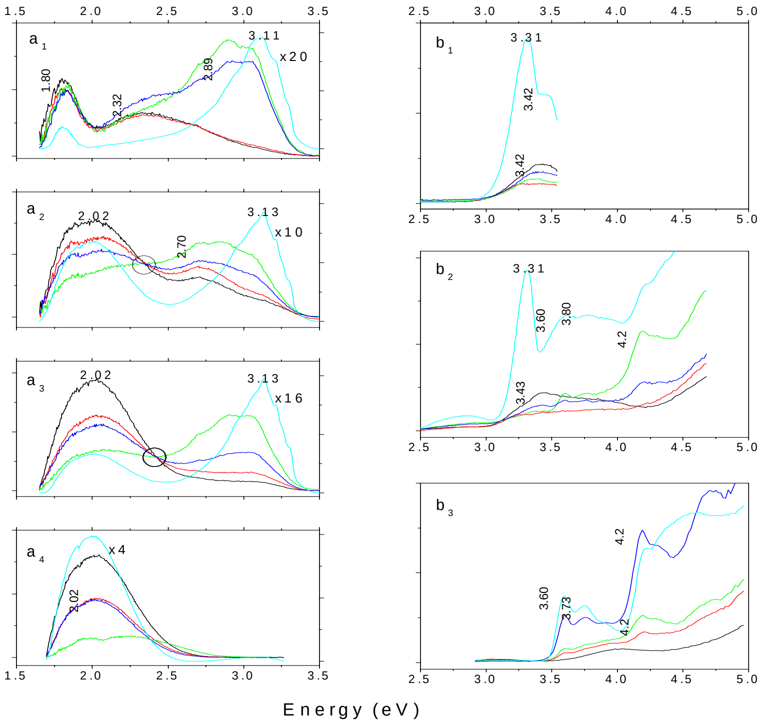

Fig. 3. PL spectra of ZnO powder hydrothermally prepared measured at RT in air (black), vacuum after two hours of pumping (red , in vacuum after two hours of heat treatment at 150 ^{0}C (green) and again in air (blue) at different excitation wavelengths 275 (a_1), 310 (a_2), 335 (a_3) and 366 nm (a_4). The cyan curves are the spectra recorded a LNT. In figures b_1, b_2 and b_3 are presented the excitation spectra for the emission band at 1.8 eV, 2 eV and 2.7 eV respectively.

Excepting the intensity, these are similar so that in the Fig. 3 were presented only the latter, (cyan curve). As common fact, on the Figs. 3 a_2 and a_3 showing the PL spectra under excitation light of 310 and 335 nm, one remark an intense emission band at 2.02 eV very sensitive to the change of measuring conditions. The intensity decrease when the sample is submitted to a vacuum thermal desorption treatment, indicates that this band originates in the adsorbed molecular film on the ZnO nanoparticles. Appealing to Fig. 2 one can imagine that at the beginning, after a moderate desorption treatment the molecules situated in the zone 2 are largely removed so that in the PL spectra one observe an increased roll played of the molecules situated in the zone 1, which are intimately bound on the nanometric particle. Such an effect is intercepted on Figs. 3 a_2 and a_3. A relative increasing of the blue (2.7 eV) and violet (2.9 eV) emission bands is made at the expense of the diminishment of green band (2.02 eV). The modification in this sense of the PL spectra becomes more evident heating of the sample in vacuum at 150 ^{o}C. The implication change of the clothing zone 2 and 1 in generating of the luminescence of ZnO nano-particles is noticed by an isobestic point where-through pass all spectra measured after different desorbtion treatment. After the desorbtion treatment, the recovery of the clothing zone 2 is noticed in the PL spectrum by an increase of the green band (2.02 eV) accompanied of the decrease of the blue (2.7 eV) and violet (2.9 eV) bands.

Different PL spectra are obtained at exciting light of 275 nm (4.5 eV) and 366 nm (3.38 eV), Fig. 3 a_1 and a_4, respectively. In the former case when the excitation energy is much higher than the fundamental absorption edge (3.37 eV), free carriers (holes and electrons) of higher kinetic energy higher than *kT* are generated, which diffusing independently through the lattice are finally trapped on the lattice defects. Afterwards, they recombine radiatively generating a PL emission or non-radiatively. Such a trapping level, related more of the volume properties, has to be less sensitive to a desorption process. Indeed, the Fig. 3 a_1 shows a PL band at about 1.8 eV less dependent on the desorption treatments. Things evolve differently when the excitation energy is little above of the fundamental absorption edge i.e. 366 nm (3.38 eV). In this case, the excitons and mutual bond electron-hole pairs formed of kinetic energy slightly lower than *kT* drift through the lattice shortly before being trapped. The penetration depth of exciting light being shorter, the traps involved in such a recombination process have to relate more the surface of ZnO nanoparticles. In this case, is quite explainable why in the in the Fig. 3 a_4 one find the same wide emission band at about 2.02 eV, varying similarly at the change of the measuring conditions as is shown in Figs. 3 a_2 and a_3.

The different involvement of volume and surface traps in the PL generation of ZnO nanoparticles may be observed following up the excitation spectra associated with different emission bands. Thus, Fig. 3 b_1 shows that in the excitation spectrum of the emission band at 1.8 eV one find only one peak at 3.42 eV when the recording is done at RT and two peaks at 3.31 and 3.42 eV for the recording at LNT. The value of 3.31 eV is associated with the excitonic transition and the 3.42 eV with the band-to-band transition. The deduction is strongly supported by the PL spectrum recorded at LNT, Fig. 3 a_1, where the two main PL bands, at 1.8 eV and 3.11 eV result from the radiative excitons recombination involving the volume and surface traps, respectively. The excitation spectrum of the wide green band, peaking at 2 eV (Fig. 3 b_2), display additional peaks at 3.6, 3.8 and 4.2 eV, not directly associated with the band gap transitions in the ZnO material, indicates the existence of luminescence centers situated in the clothing of ZnO nano-particles.

A similar presentation of the emission and excitation spectra for the hydrothermally synthesized ZnO/SWNTs composites is given in Fig. 4. As above the PL spectra were recorded at four excitation wavelengths, 275, 310, 335 and 366 nm. One observes that the intensity of the wide green band greatly vary if the measurements were performed with the sample in air or after a desorption treatment. The sensitivity to a desorption treatment proves that this band mainly originates in the luminescence centers situated in the clothing zone 2. Different is the behavior of PL spectra in the high energy range, where one find the bands peaking at 2.7 and 3.12 eV. No isobestic point and no great variation of intensity is observed in this case. This suggests a different implication in the PL process of the clothing zones 1 and 2. The former zone that involves stronger bounds with the ZnO particle is changed due to the intimacy binding between the ZnO particle and SWNTs. According to expectations, the contribution to the luminescence spectra of the bands at 2.7 and 3.12 eV remains fixed regardless the measurement conditions and the variation of the green band, Fig. 4 a_2 and a_3. Comparing the PL spectra presented in Fig. 3 a_2, a_3 and Fig. 4 a_2, a_3 one observes immediately that the relative intensity of the band at 3.12 eV is much weaker in the case of ZnO/SWNTs composite.

Such a result proves the quenching roll of SWNTs. [14]. From the variation the PL spectra of ZnO and ZnO/SWNTs composite with the experimental measuring conditions results that the most sensitive is the green band at about 2.0 eV and referring to the Fig. 2 we are tempted to consider its origin in the second clothing of the ZnO nanoparticle. The different behavior of the bands situated in the PL spectrum towards higher energies (2.35, 2.7, 2.9, 3.12 eV) pled for their origin in the inner clothing zone where the interactions between the ZnO core and adsorbed molecules are stronger.

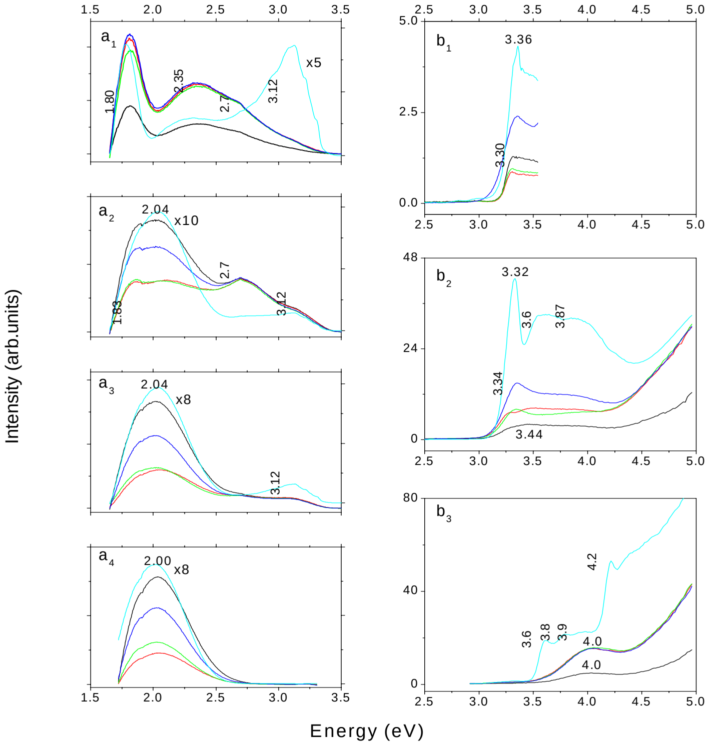

Fig. 4. PL spectra of ZnO/SWNTs composite hydrothermally prepared measured at RT in air (black), vacuum after two hours of pumping (red), in vacuum after two hours of heat treatment at 150 ^{0}C (green) and again in air (blue) at different excitation wavelengths 275 (a_1), 310 (a_2), 335 (a_3) and 366 nm (a_4). The cyan curves are the spectra recorded a LNT. In figures b_1, b_2 and b_3 are presented the excitation spectra for the emission band at 1.8 eV, 2 eV and 2.7 eV respectively.

Here are formed various surface luminescence sites that behave differently in comparison with the base materials. A first difference is that these new luminescence sites can be activated with light of different energy than corresponding to the band-to-band transition in the ZnO nanoparticle. Such a situation is revealed in Fig. 3 b_3 and Fig. 4 b_3 where are shown the excitation spectra associated with the blue PL band at 2.7 eV (460 nm). In this case one the optimum excitation of the blue band occurs for an exciting light of higher energy that the band gap of ZnO. Related to this result, another point of view could be invoked: if the PL band at 2.7 eV is directly related with the size of ZnO nanoparticle, then its excitation spectrum shifted towards higher energies illustrates a band gap broadening through the diminishment of the particle size.

4. Conclusions

This paper reports new results obtained by photoluminescence (PL) studies on ZnO and ZnO/SWNTs composites prepared by hydrothermal route. Our results allow to draw the following conclusions: i) PL spectra of nanometric powder are dramatically influenced by the adsorption of different molecules coming from the environment. The perturbing effect is much decreased if samples are submitted previously to desorption heat-treatment at 150 ^{o}C performed in vacuum; ii) a partial quenching of PL is observed as increasing the SWNTs weight in the synthesis mixture; iii) PL spectra of the ZnO/SWNTs composites are characterized by a emission band with a maximum at 405-450 nm.

Acknowledgments

Work performed in the frame of the Scientific Cooperation between the Institute of Materials in Nantes and the Laboratory of Optics and Spectroscopy of the National Institute of Materials Physics in Bucharest. This work was supported by NATO reintegration grant RIG-981483 and Romanian research project No.2-CEx-06-11-95/25.07.2006.

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