



Synthesis and properties of the nanocomposite of zinc oxide and poly(amic acid)

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Abstract

The composite comprised of zinc oxide quantum dots and poly(amic acid) (PAAc) was prepared and studied by X-rays diffraction, X-ray photoelectron spectroscopy, light scattering, UV absorbance and UV fluorescence. The UV absorbance of the ZnO/PAAc composite was found to be much larger than that of its components taken separately. The fluorescence of the ZnO/PAAc composite was found to be shifted to longer wavelengths in comparison with pure ZnO. The presence of the dopant dodecylbenzenesulfonic acid was found to affect the observed fluorescence.

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1. Introduction

Quantum dots are a new class of nanomaterials that have quasi one-dimensional properties. Two examples of materials that can be obtained in the form of quantum dots are zinc oxide (ZnO) and cadmium sulfide (CdS). ZnO quantum dots have attracted much attention because they do not present a health hazard and can be relatively easily obtained, for example, by sol–gel synthesis [1], chemical precipitation [2], colloidal synthesis [3] and electrophoretic dissolution of a sacrificial anode [4,5]. During the past decade ZnO has been extensively studied as a potential material for

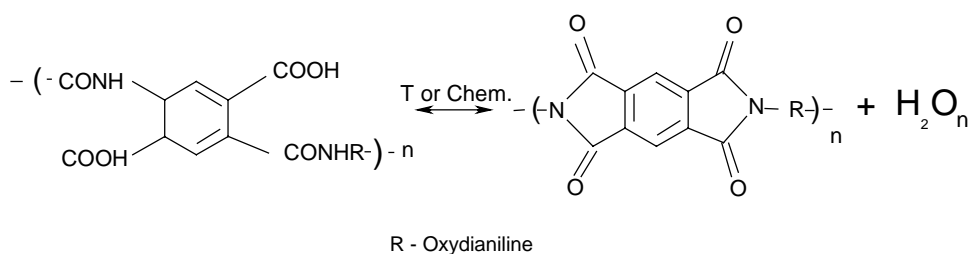
acoustic wave devices [6], photonic devices for the UV spectral region [7] and as an excellent material for UV protection [8]. Combining ZnO nanoparticles with a polymer was shown to modify its optical properties. ZnO/polymer composites have been produced with different polymer matrices, such as poly(vinylpyrrolidone) [9] and poly(methylmethacrylate) [10]. The polyimides (PIs) have attracted a lot of interest for photonic applications because of their conjugated π -electron system. Moreover, they possess excellent dielectric properties, outstanding thermal and chemical stability and low coefficients of thermal expansion [11]. These attributes make the ZnO/PI composite material a potentially interesting one for photonic applications in the UV region of the spectrum. In the research reported here ZnO nanoparticles were combined with polyamic acid (PAAc) and their properties were investigated. PAAc of PI Pyromellitic Dianhydride Oxydianiline was used. The PAAc is a

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soluble PI precursor and its conversion to PI can be achieved by the imidization reaction (cyclic dehydration) [12] shown below.



2. Experimental

2.1. Synthesis

ZnO nanoparticles were obtained electrochemically by dissolving a zinc sacrificial anode based on a technique that was described earlier, for example, in ref. [5]. A dodecylbenzenesulfonic acid (DBSA) sodium salt (Aldrich grade) at a concentration level of 0.1 M was dissolved in acetonitrile/tetrahydrofuran 1:4 solution and served as the dopant and electrolyte. The reaction was performed in the galvanostatic regime in a one-compartment electrochemical cell that is shown in Fig. 1. The electrochemical cell consisted of a zinc anode, a stainless steel counter electrode and a saturated calomel reference electrode (SCE). The mass rate of ZnO formation was 1.88×10^{-6} g/s at current 1 mA. The reaction lasted

from 6 to 12 h. After the reaction was completed, the ZnO particles were precipitated by centrifugation. To obtain a solution of the ZnO/PAAc composite, the

precipitant was mixed with a 10% (by volume) PAAc solution in dimethylacetamide (DMAc) by ultrasonication. The smallest particles were separated from the others by centrifugation at 300 rpm. To obtain the desired ZnO suspension in DMAc, the precipitate was carefully separated from the primer solution and redispersed.

2.2. Apparatus

The particle size distribution was determined using a MASTERSIZER apparatus manufactured by Malvern Instruments, and X-ray photoelectron spectroscopy (XPS) measurements were performed on a LH X1 Leybold spectrometer. The absorbance was measured on a Shimadzu 2010 UV Spectrophotometer and X-ray diffraction spectra were obtained with a Philips X'pert Diffractometer. Finally, UV fluorescence at an

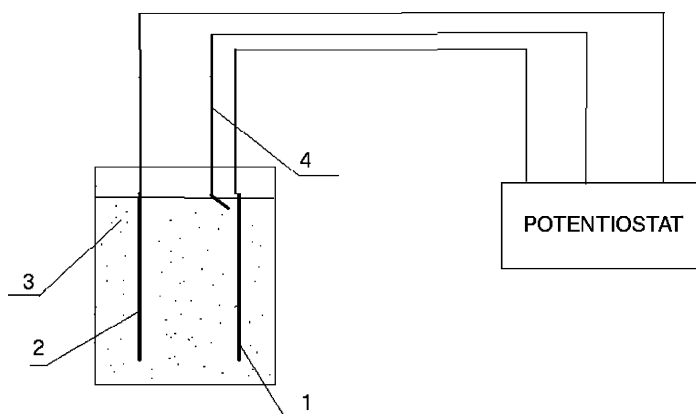


Fig. 1. Schematic representation of electrochemical cell used to produce ZnO nanoparticles. (1) Working electrode; (2) counter electrode; (3) solution; (4) reference electrode (SCE).

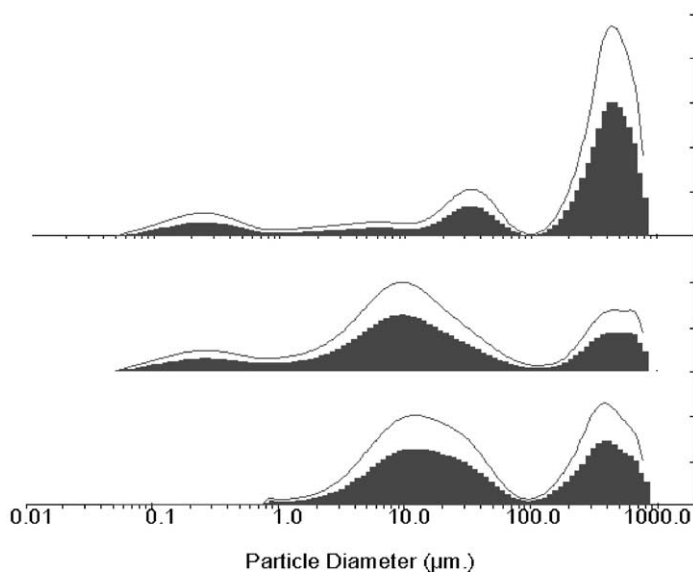


Fig. 2. Particle diameter as a function of current density, from lower to upper: 2, 5 and 10 mA/cm².

excitation wavelength of 250 nm was measured by using a Perkin-Elmer Luminescence Spectrometer model LS50B.

2.3. Particle size distribution

The concentration of the sample was selected to fall between 1 and 3.5% in ethanol solution. Fig. 2 shows the particle size distribution of the ZnO powder obtained at different current densities, at samples area 1 cm². Fig. 2 indicates the presence of essentially three distinguishable groups of particles: small ones ($\leq 0.2 \mu\text{m}$), medium (10–12 μm) and large (130–150 μm). The 10 mA cell current regime gave the largest fraction of the smallest particles.

3. Results and discussion

3.1. X-ray diffraction

The samples used for XRD and XPS measurements were ZnO/PAAc suspensions that were dried by evaporating the solvent on the surface of a glass plate. Fig. 3A shows the XRD images of pure PAAc. It has a broad peak that is characteristic of amorphous polymers.

Dried ZnO powder produces only sharp peaks. The identification of these peaks is presented in Fig. 3B. Fig. 3C displays the XRD image of the ZnO/PAAc composite. The PAAc produces a broad peak centered at 20°. In the ZnO/PAAc composite characteristic the ZnO peaks (planes 1 0 0, 0 0 2, 1 0 1, 1 0 2, 1 1 0, 1 0 3, 2 0 0, 1 1 2 and 2 0 1) are marked with the cross symbol. The new peaks were attributed to the DBSA. The decrease in the intensity of the crystalline peaks indicates that the structure had become more amorphous.

3.2. X-ray photoelectron spectroscopy

Fig. 4 presents the Auger spectra for the ZnO/PAAc composite. The Auger spectrum for oxygen indicates that the oxygen was present in both the uni-valent (O^-) (530 eV) and bi-valent (O^{2-}) (532 eV) states [13], and this confirms the presence of oxygen vacancies in the system studied here. The Auger spectrum for zinc shows the presence of the 1022.5 eV peak for Zn^{4+} and the 1023 eV peak for Zn^{2+} . The peaks at 1023, 1025 and 1026.4 eV found for the ZnO were shifted relative to their commonly reported values (largest 1022.2 eV) while the spacings were preserved. The origin of this shift is not clear.

3.3. Absorbance

The absorbance of a non-doped ZnO suspension is shown in Fig. 5. The curve has a non-abrupt absorption edge varying over a range of 335–360 nm. The ZnO is a semiconductor with a band gap energy of 3.4 eV that

is responsible for the absorption in this range. The addition of the PAAc chains causes the changes in the shape of the absorbance curve. The presence of just 2% of PAAc shifts the red boundary to 370 nm. The same effect was observed in a PAAc solution without ZnO but with an increased PAAc concentration (see Fig. 6).

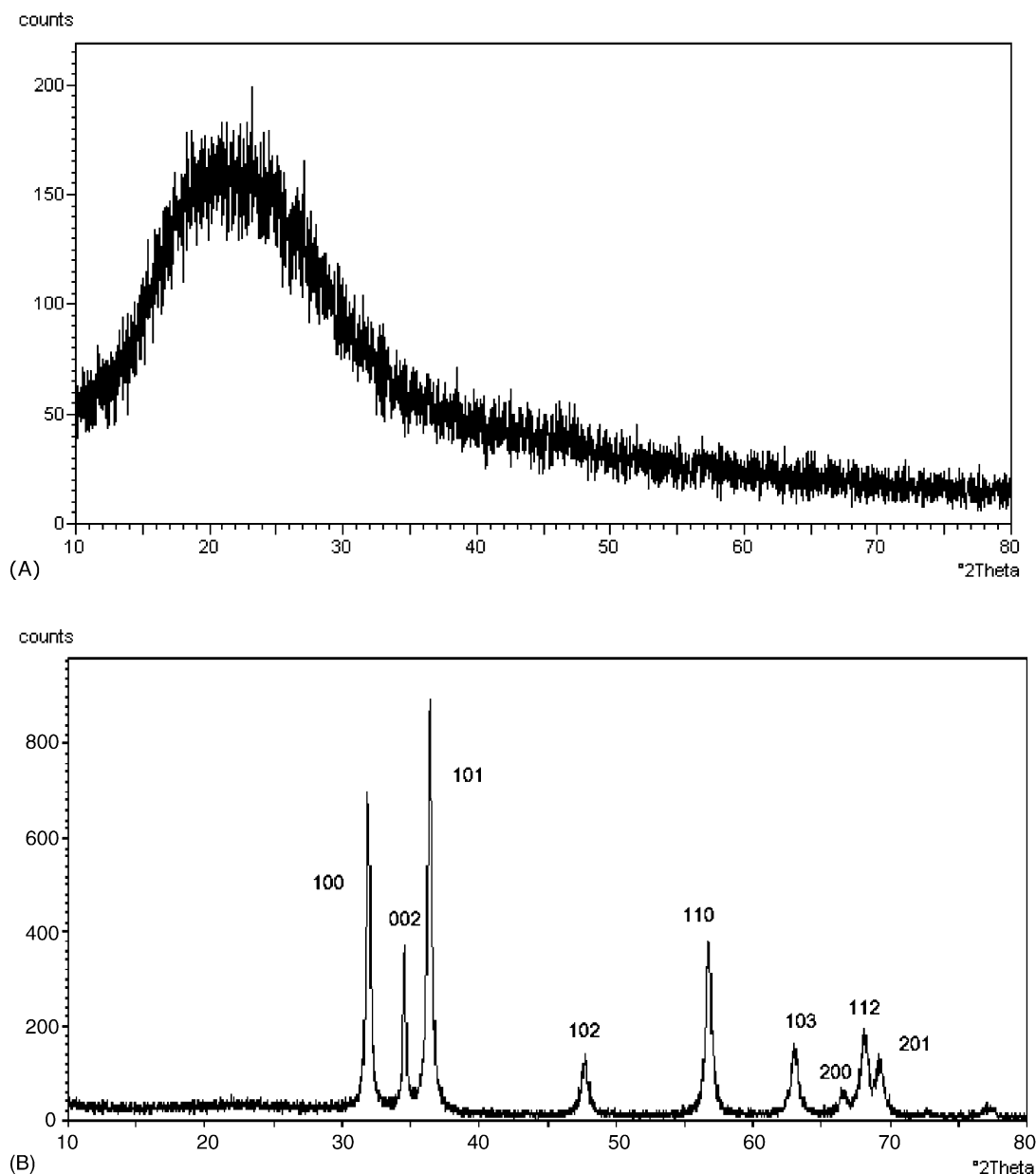


Fig. 3. XRD patterns of (A) pure PAAc, (B) pure ZnO and (C) the ZnO/PAAc composite.

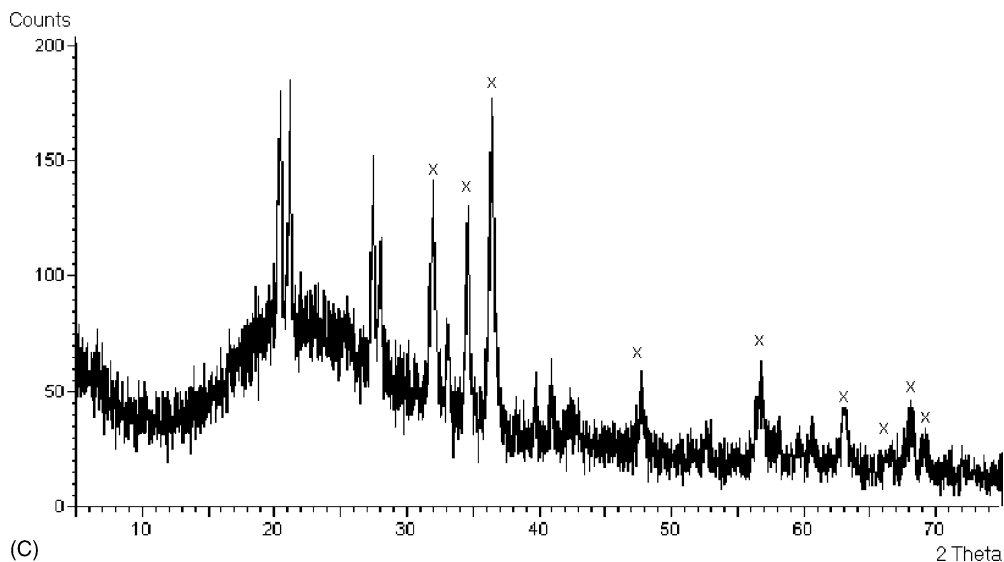


Fig. 3. (Continued).

PAAC displays absorbance in the UV region due to its delocalized π -electrons [11]. There is no essential change in absorbance produced by the addition of aliquots of PAAC solution to non-doped ZnO suspen-

sions (see Fig. 7). However, there was a large change in absorbance produced when small amounts of PAAC solution were added to a suspension of DBSA doped ZnO with the same particle concentration (see Fig. 8).

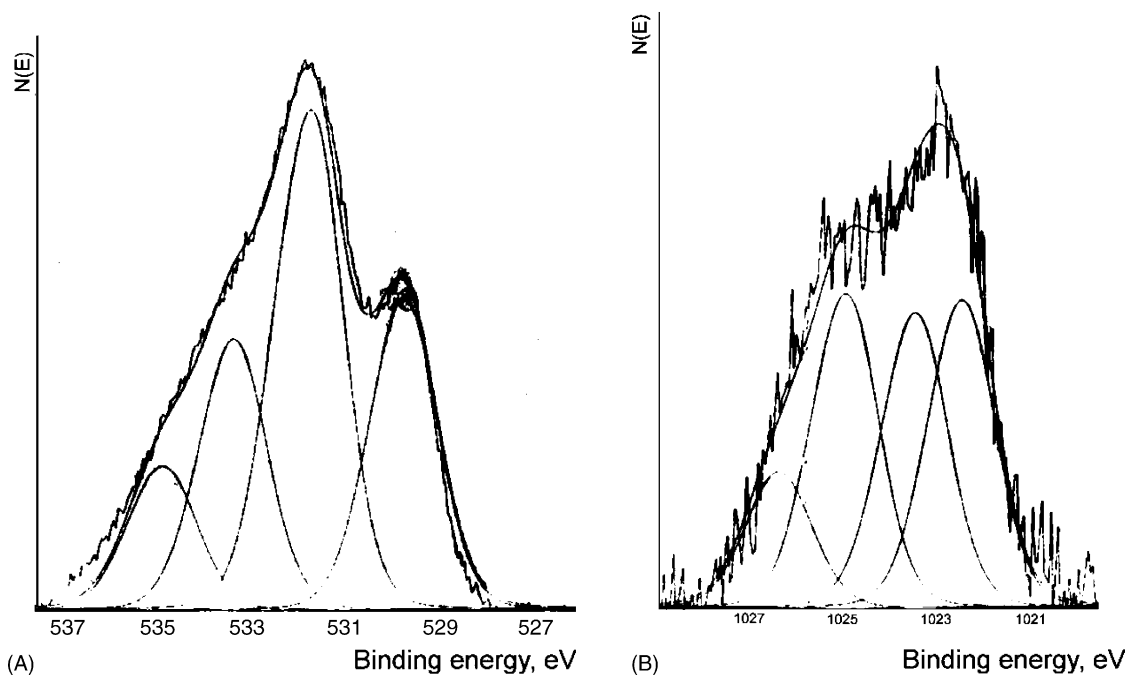


Fig. 4. XPS images of the ZnO/PAAC composite: (A) oxygen 1s electron and (B) zinc 2p3 electron.

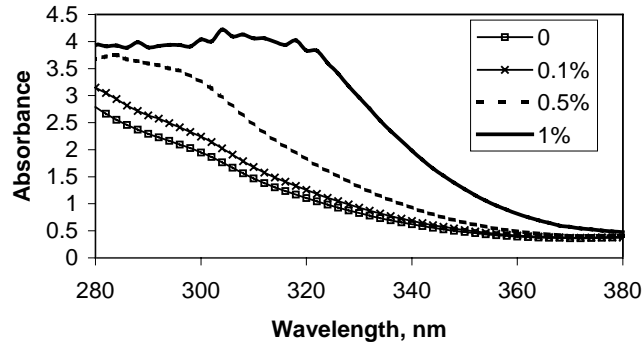


Fig. 5. Absorbance of undoped ZnO in DMAc solution containing PAAc at different concentrations. PAAc was added from a 10% solution in different amounts.

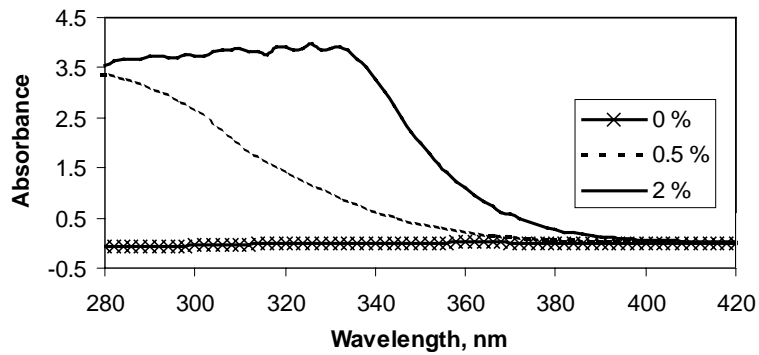


Fig. 6. Absorbance of PAAc in DMAc solution at different concentrations of PAAc.

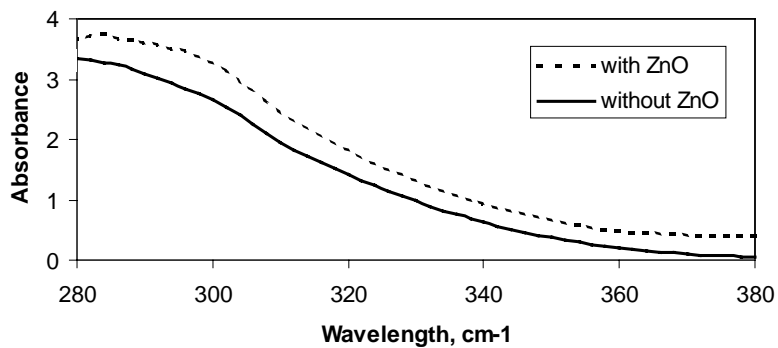


Fig. 7. Influence of ZnO on the absorbance of 0.5% PAAc solution in DMAc.

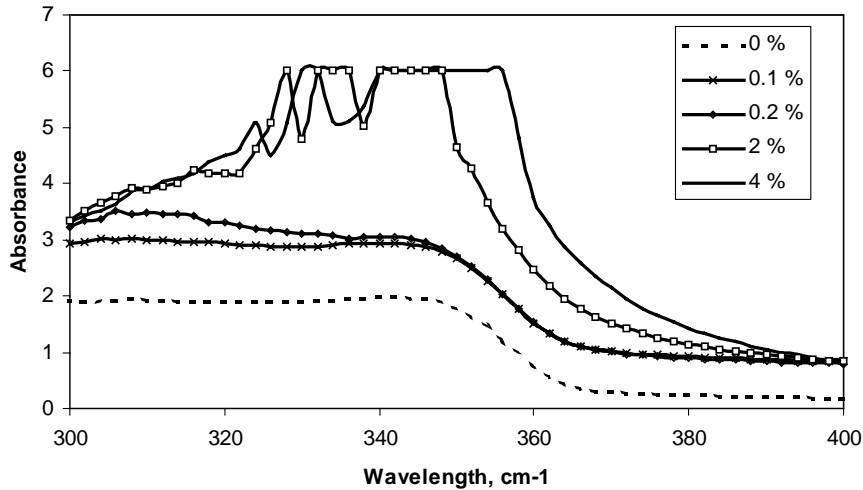
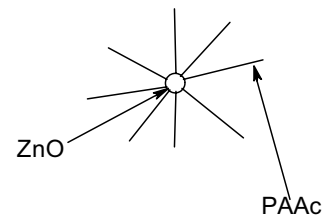


Fig. 8. ZnO (F) produced at 5 mA/cm² in DMAc after addition of droplets of 10% PAAc solution in DMAc.

The addition of 2–4% PAAc solution caused a large increase in absorption (by more than three orders of magnitude). This is possibly a consequence of the result that in a solution containing ZnO and PAAc the ZnO nanoparticles are surrounded (or ‘capped’) by PAAc molecules as shown in Scheme 1. The abnormal absorbance of the doped ZnO capped by PAAc is possibly caused by very effective photon trapping by the bandgap of a quantum dot in a polymer ligand environment. A detailed mechanism for this phenomenon cannot be given at this time because the electronic states in the quantum dots are not as well understood as the molecular electronic states. The mechanism for the reaction between the carbonyl and hydroxyl groups on the Zn surface that leads to the surface bonded hydroxalate groups is considered to explain the capping effect.

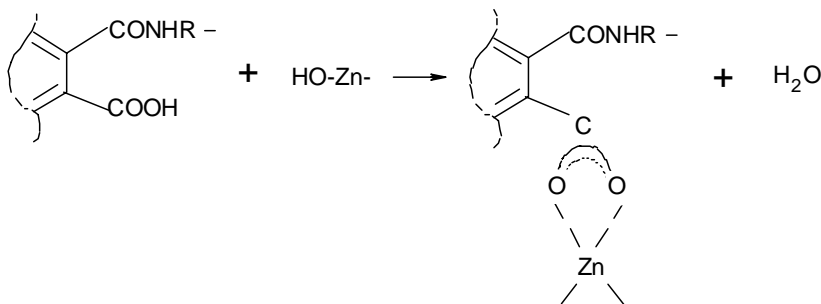


Scheme 1.

3.4. Fluorescence

3.4.1. Doped ZnO

A shift in the fluorescence peak from 380 to 440 nm was observed when DBSA doped PAAc was added to a ZnO suspension (see Fig. 9). This probably corresponds to the shift in the level of the oxygen vacancies



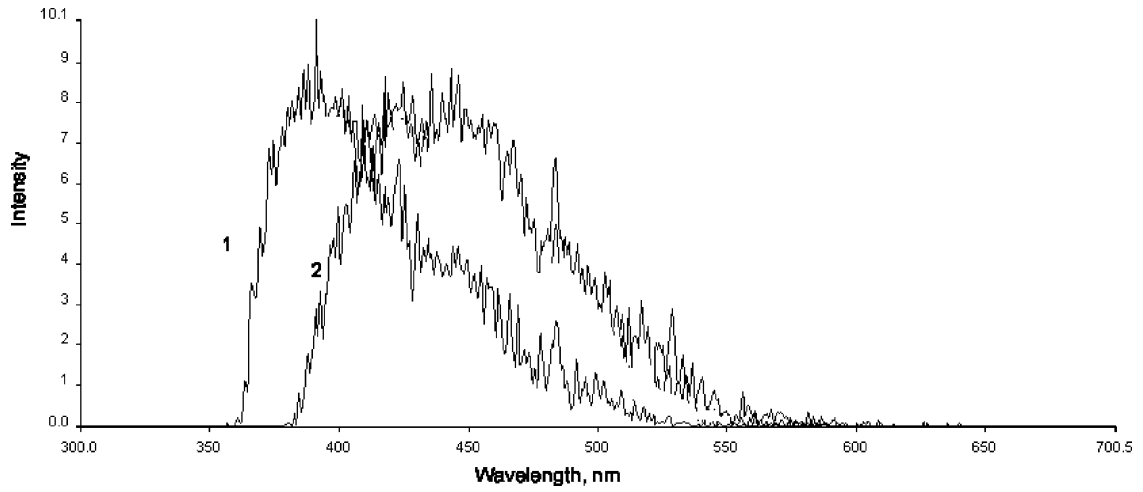
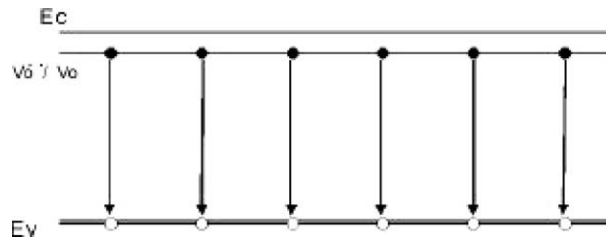


Fig. 9. ZnO doped with DBSA in DMAc (curve 1) and after the addition of 5% of PAAc solution (curve 2).



Scheme 2.

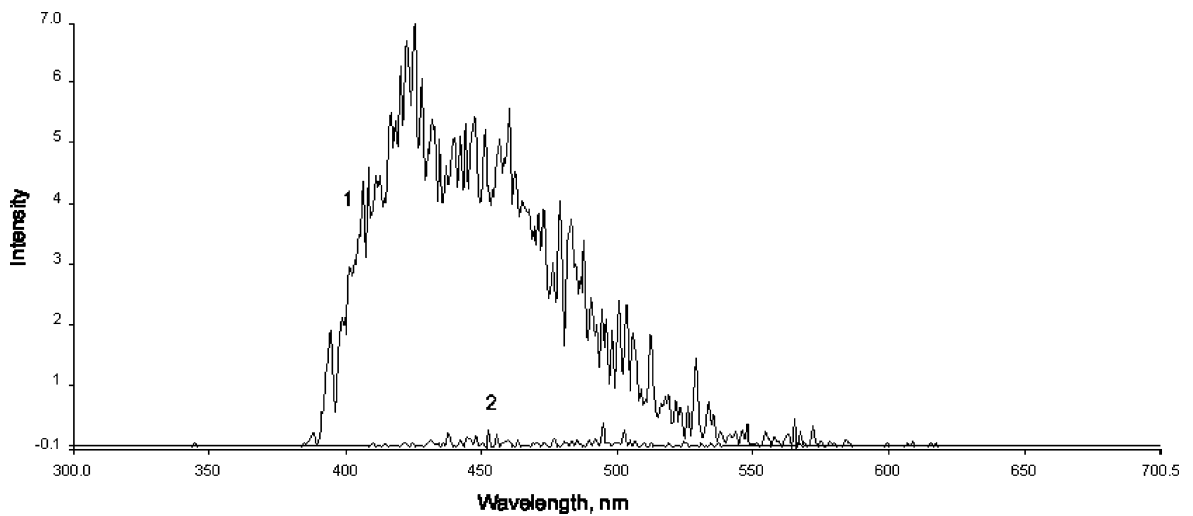


Fig. 10. ZnO doped with DBSA in DMAc with 10% PAAc (curve 1) and 25% PAAc (curve 2).

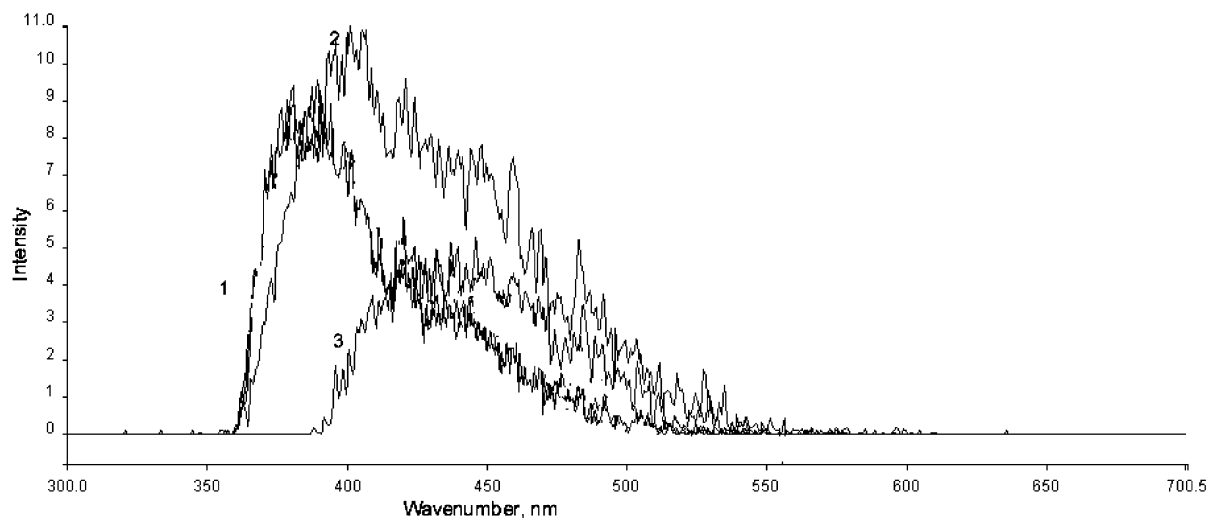


Fig. 11. Undoped ZnO: without PAAc (curve 1), with 5% of PAAc solution (curve 2), and 25% of PAAc solution (curve 3).

closer to E_v (see Scheme 2) caused by changes in the dimensions of the quantum dots. Further, broadening and then final quenching was observed when the amount of PAAc reached 25% (see Fig. 10). At the 10% PAAc peak the spectrum becomes bimodal with two positions of maxima at 415 and 460 nm that is related to changes in the quantum dot zone structure in the ligand molecular neighborhood. Quenching of the luminescence is possibly correlated with the increased absorbance discussed above (Fig. 10).

3.4.2. Undoped ZnO

Quenching of the fluorescence is less strong for the undoped ZnO (see Fig. 11). Peak is also shifted to lower wavelengths at low PAAc concentrations.

4. Conclusion

The absorbance of doped ZnO was found to increase dramatically when 2–3% of PAAc solution was added to a ZnO suspension, possibly due to strong capping of the Zn atoms by linear organic chains. The shift of fluorescence to longer wavelengths was observed as a consequence of the PAAc addition. This work shows that it is possible to vary (or tune) the fluorescent and absorbance properties of the ZnO/PAAc nanoparticle suspension by the addition

of an appropriate amount of dopant of low molecular weight.

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