Growth and characterisation of ZnO quantum dots in polyacrylamide

N.O. Dantas\textsuperscript{a}, A.F.G. Monte\textsuperscript{b,\ast}, W.A. Cardoso\textsuperscript{a}, A.G. Brito-Madurro\textsuperscript{c}, J.M. Madurro\textsuperscript{c}, P.C. Morais\textsuperscript{b}

\textsuperscript{a}LNMIS, Faculdade de Física, Universidade Federal de Uberlândia, 38400-902 Uberlândia-MG, Brazil
\textsuperscript{b}Núcleo de Física Aplicada, Instituto de Física, Universidade de Brasília, 70919-970 Brasília-DF, Brazil
\textsuperscript{c}Instituto de Química, Universidade Federal de Uberlândia, 38400-902 Uberlândia-MG, Brazil

Available online 24 March 2005

Abstract

ZnO nanocrystals were successfully fabricated by wet-chemical method. Optical properties of excitons confined in ZnO nanocrystals were studied by measuring both optical absorption and photoluminescence spectra. Absorption due to free excitons was clearly observed whereas strong PL lines were recorded in the UV region at around the exciton absorption energy. Red-shift of optical features with increasing annealing time indicates an increase in quantum dot size.

© 2005 Published by Elsevier Ltd.

PACS: 61.41.+e; 61.46.+w; 61.82.Rx; 73.61.Tm; 82.70.Dd

Keywords: ZnO; Nanocrystals; Polyacrylamide; Quantum dots; Optical properties

1. Introduction

In the recent years, the wide band-gap ZnO semiconductor has attracted considerable attention due to the development of optoelectronic devices such as ultraviolet light-emitting diodes, solar energy conversion, and lasers [1–3]. Alternatively, magnetic ion-doped ZnO quantum dots (QDs) have been targeted as promising candidates for the implementation of novel technologies, such as in spintronic and quantum computation [4]. Electronic structure and magneto-optical properties of ZnO QD structures have been intensively studied both theoretically and experimentally [5]. However, the control of the dot size and size dispersity is a great challenge for nanocrystal production, since both size and surface characteristics have considerable effects upon optical and magnetic properties of QD structures [5].

In this study, we describe a simple method for producing ZnO nanoparticles. The ZnO nanoparticles were synthesized via wet-chemical method and post-growth annealing treatments. Optical properties were investigated as a function of the annealing times. The optical absorption peaks shift to lower energies as the annealing time increases, since this process reduces the quantum confinement by increasing the nanocrystal size.

2. Sample and experiment

All employed chemicals were used as received without further purification. The chemicals were purchased from different companies: acrylamide 99.9% (Bio-Rad), bisacrylamide 98% (Sigma), zinc oxide 99% (Vetec), ammonium persulfate 98% (Invitrogen), and TEMED (N,N,N',N'-tetramethylenediamine) 99% (Sigma).

ZnO nanoparticles were prepared in suspension with deionized water, using the following concentrations: 0.2, 0.5, and 1 mmol/L. The suspension was immersed in ultrasound bath during 1 h for homogenization. For the copolymerization reaction 100 mL of a mixture containing acrylamide (0.506 mol) and bisacrylamide (6.36 mmol) was prepared. The ZnO solution was added slowly to the jelly monomer mixture. Ammonium persulfate (10%) and TEMED were added to the jelly matrix, allowing the copolymerization reaction to take place at room temperature. The samples were stored at room temperature for aging in normal atmosphere or in vacuum. After aging for 30 days, sample annealing was carried out at 50 °C, during 1 and 4 h.
The best results were obtained with samples aged in vacuum.

The obtained ZnO nanoparticles were characterized by using optical absorption (OA), photoluminescence (PL). Room-temperature OA-spectra were obtained using a spectrophotometer Varian-500 operating between 250 and 1000 nm. Photoluminescence was realized using a Xenon-lamp as excitation source whereas detection was carried out using a silicon photodiode attached to a single spectrometer.

3. Results

The aging and the annealing processes of the prepared samples were monitored using room-temperature OA spectroscopy. Fig. 1 shows the evolution of the absorbance spectra of the synthesized ZnO nanoparticles. All the spectra show well defined exciton absorption peaks, characteristic of ZnO nanoparticles, which have a significant blue-shift as compared with the ZnO bulk (3.29 eV), indicating that the average particle sizes are in the quantum size regime. Notice from Fig. 1 that the absorption onset shifts to the lower energy side of the spectrum as the sample was aged, indicating the growth (aging) of primary nanoparticles. Fig. 1 also shows the red-shift of the ground exciton state with increasing annealing time, indicating an increase of nanoparticle size.

The ZnO nanoparticles exhibit band-to-band absorption at 4.3 eV, whereas bulk ZnO shows excitonic absorption at 3.29 eV. Using this information, the nanoparticle sizes were determined from the absorption onset by the effective mass model approximation [6]:

\[
E \equiv E_{\text{bulk}} + \frac{\hbar^2 \pi^2}{2er^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right)
\]

where \(E\) is the band gap of the nanoparticles, \(E_{\text{bulk}}\) is the band gap of the bulk material, \(r\) is the particle radius, \(m_e\) and \(m_h\) are effective masses of the electrons and holes, respectively, and \(m_0\) is the free electron mass. With the effective masses of electrons (\(m_e = 0.28 m_0\)) and holes (\(m_h = 0.59 m_0\)), we obtain 2.46 nm (diameter) for the as-prepared nanoparticles. The corresponding diameter of aged ZnO nanoparticles with different annealing times was estimated in 2.7 nm for annealing at 50 °C during 1 h. For the nanoparticles annealed during 4 h, the average diameter was 3.0 nm.

Fig. 2 displays the photoluminescence spectra of the ZnO nanoparticles. Xenon lamp was used as the light source by exciting the sample at 260 nm. A green emission peak and a UV peak were observed in the PL spectra. The UV emission is assigned to recombination of bound excitons. On the other hand, the green emission mechanism in ZnO has been extensively investigated [7]. Singly ionized oxygen vacancy results in green emission of ZnO material because of recombination of a photogenerated hole with a singly ionized electron in the valence band [8]. The increase in the UV–visible emission ratio indicates an improvement of the crystal quality of the nanoparticles, i.e. a decrease in the density of surface defects that may happen during the aging and the annealing processes. Also, blue-shift in UV emission peak position compared with that estimated for the bulk ZnO is due to the quantum confinement effect. The extent of this blue shift decreases as the size of the primary particles increases during the aging and annealing processes.

4. Conclusion

ZnO nanocrystals were successfully fabricated by wet-chemical method. PL spectra observed in the UV region demonstrates the nanoparticle emission corresponding to the exciton absorption energy. Red-shift of optical features with increasing annealing time and aging indicates an increase in the QD-size.
Acknowledgements

We acknowledge financial support from FAPEMIG and CNPq (Brazilian Agencies).

References


