

Structural and optical characterization of CdS nanocrystals embedded in polystyrene matrix

B. HARIECHE^{a*}, B BOUDINE^a, O. HALIMI^a, A. FISCHER^b, A. BOUDRIOUA^b, M. SEBAIS^b

^aLaboratoire de Cristallographie, Département de Physique, Faculté des Sciences, Université Mentouri – Constantine, Route Ain El Bey 25000 Constantine Algeria

^bLaboratoire de Physique des lasers, CNRS – UMR 7538

Institut Galilée, Université Paris 13, Avenue Jean Baptiste Clément- F 93430 Villetaneuse, France

Cadmium sulfide (CdS) nanocrystals embedded in polystyrene matrix were successfully prepared by dispersing the CdS nanosize powder in polystyrene matrix. The structural characterization was performed by X-ray diffraction. The CdS nanocrystals are single crystals of wurtzite phase. The particle of the CdS nanocrystals embedded in polystyrene has nanometric size. The room temperature UV-visible absorption spectra show a shift towards higher energies of the absorption edge. Raman spectra exhibit the longitudinal optical phonon mode (LO) characteristic peak of CdS. The room temperature luminescence is formed by one band situated at 2.50 eV. This band is attributed to a band-to-band transition.

(Received January 24, 2011; accepted June 9, 2011)

Keywords: CdS nanocrystals, polystyrene, Absorption, Luminescence and Micro-Raman

1. Introduction

Recently, nanocrystalline large band gap semiconductors, embedded in various materials, arise a special interest. This research effort is stimulated by the interesting properties that appear as size decreases. Indeed, confinement of excitations to a narrow space is then observed [1, 2]. Intensive research is conducted in order to fabricate nanocrystals having a desired size and shape [3], and to understand the influence of the fabrication conditions [4] and the host matrix on the properties of the nanocrystals [5].

CdS nanocrystals find application in several fields, especially in opto-electronics [6]. CdS based luminescent diode emitting blue light and solar cells have already been developed [7, 8]. By adjusting the fabrication conditions, it is possible to obtain nanocrystals with a very weak size distribution and thus obtain a quasi-monochromatic emission in the ultra-violet range when size is sufficiently small. With this view, several techniques have been used to prepare nanocrystals. Among these are embedding nanocrystals in crystalline matrices using the Czochralski method [9-10], in monolith using sol-gel method [11-12], in an aqueous solution using chemical techniques [13]. M. Mukherjee et al. [14] have synthesized the nanocrystalline CdS particles. The obtained nanocrystalline CdS particles have been dispersed in polystyrene matrix in the form of thin composite film. Xinjian Cheng et al. [15] have prepared nano-CdS/polystyrene composite particles via surfactant-free emulsion polymerization. The UV-vis absorption and fluorescence measurement indicated the quantum dot effect in the resulted nano-CdS/PS composite particles. Milena Marinovi Cincovi et al. [16] have explained that the polystyrene matrix blocked the surface

states that promote radiation less recombination, resulting in enhanced band-to-band luminescence of CdS quantum dots. Recent works [17] have showed the Incorporation of CdS nanoparticles into the polyacrylonitrile (PAN) matrices. The obtained composite exhibits an induced positive nonlinear absorption of incident light. The choice of the matrix is important for specific applications because the environment of the nanocrystal greatly influence behavior.

The present work presents the fabrication of CdS nanocrystals embedded in polystyrene matrix using the spin-coating method. Structural characterization is achieved though XRD and micro-Raman spectroscopy, while the optical properties are determined using optical absorption and photoluminescence.

2. Experimental procedure

Polystyrene is dissolved in chloroform (CHCl₃). To the resulting solution are added CdS nanocrystals obtained by ball milling method [18]. The solution is homogenized by magnetic agitation for 24 h, and polystyrene – CdS nanocrystals composite films are obtained by spin-coating method. Using syringe, a drop from the solution is deposited on a glass blade. The blade is mounted on motorized axle rotating using a speed range from 300 to 3000 rpm during 45 s; the obtained sample of polystyrene film doped with CdS nanocrystals is yellowish.

X-ray diffractograms (XRD) have been obtained using the Cu K α radiation ($\lambda_{K\alpha} = 1.5402 \text{ \AA}$ and a Ni filter with Siemens diffractometer (advanced D8) at 40 kV and 30 mA in the 2θ range ($10^\circ - 80^\circ$). Raman spectra were recorded in a back scattering configuration with a Jobbin Yvon micro Raman spectrometer coupled to a DX40

olympus microscope. The samples of the polystyrene pure film and the composite film are excited with a 632.8 nm wavelength with an output of 20mw. UV – visible spectra were recorded with Shimadzu UVPC 3001 spectrophotometer. Photoluminescence data were obtained by exciting the sample at room temperature with a 350 nm radiation generated by an Argon laser.

3. Results and discussion

The XRD diffractogram of the pure polystyrene film (Fig. 1) clearly indicates the amorphous nature of the polymer. Indeed, no diffraction peak could be detected. However, the composite of polystyrene – CdS nanocrystals film exhibits diffraction peaks corresponding to the (100) (002), (101), (110), and (103) Wurtzite CdS reflections. On the JCPDS card n° 41-1049, the most intense reflection of CdS is the (101) reflection, but on figure 2, the most intense reflection of CdS is the (110). CdS nanocrystals are thus preferentially oriented with their (110) planes parallel to the surface of the film. The shift of the peak positions towards lower angles indicates a probably contraction of the lattice parameter when the size gets very small. When size decreases, the number of surface atoms is higher than that of bulk atoms. Surface energy becomes then dominant and causes this contraction.

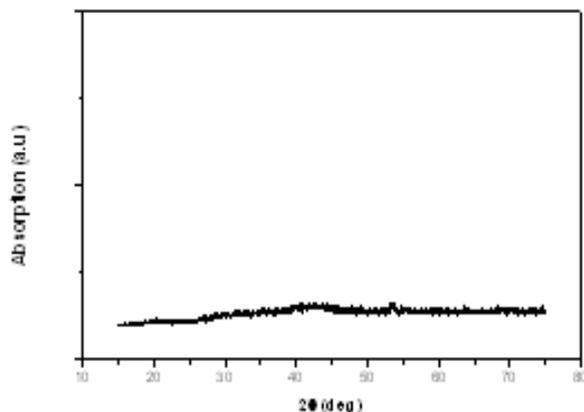


Fig. 1. Diffractogram of pure polystyrene.

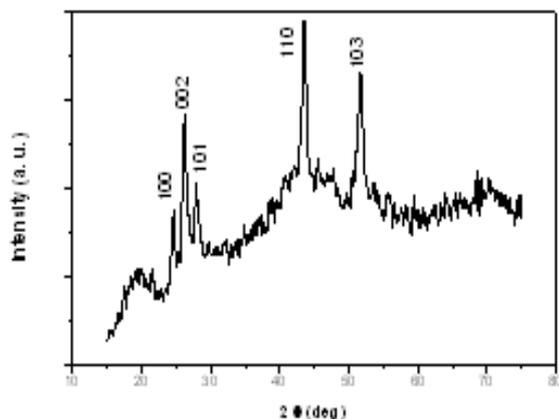


Fig. 2. Diffractogram of CdS nanocrystals – Polystyrene composite.

Assuming that the embedded crystallites are spherical, their sizes can be estimated using Scherer formula

$$d = \frac{0.9\lambda}{B(\theta)\cos(\theta)} \quad (1)$$

Where:

d: diameter of the nanocrystal.

λ : wavelength of the $K\alpha$ radiation.

$B(\theta)$: full width at half maximum (FWHM) of the diffraction peak.

θ : Bragg diffraction angle.

Table 1 summarizes the average size corresponding to each diffraction peak.

The average diameter of the CdS nanocrystals is comprised between 7.4 and 15.8 nm. The Bohr radius of the bulk CdS exciton is of the order of 3 nm [18].

Table 1: Peak diffraction positions and sizes of CdS crystallites.

2 θ	FWMH	I/I ₀ (%)	Diameter (nm)	Plane
24.62	0.52	33	15.8	100
26.20	0.71	74	11.4	002
27.93	1.22	34	7.4	101
43.51	0.65	100	13.2	110
51.63	0.83	68	10.7	103

The micro Raman spectrum of the composite (fig. 3 b) exhibits the characteristic peak of CdS. The peak at 296 cm^{-1} corresponds to the longitudinal optical phonons (LO); this peak has a 18 cm^{-1} as FWHM and a shift of 4 cm^{-1} towards lower frequencies. The shift of the peak positions towards lower frequencies in the present work is due to the quantum confinement effect which appears when size is small.

It is reported in the literature that the shape and width at midhalf height (FWHM) change when the size of crystallites decreases. P. Nandakumar et al. [19] have noticed the broadening of the 1LO peak increases when the size of CdS nanoparticles varies from 6 nm to 1.6 nm and the FWHM increases from 12 cm^{-1} at 19 cm^{-1} . They also reported that the shape of the peak (1LO), which was symmetrical for nanocrystals with 6 nm of size, is antisymmetrical for the other sizes below. For nanocrystallites, the effect of confinement leads to a broadening of the peak and shift to low frequencies in the peak position.

The other peaks are characteristic of polystyrene (cf. spectrum on fig. 2a). This result is in agreement with the work of Yu. P. Rakovich et al. [20].

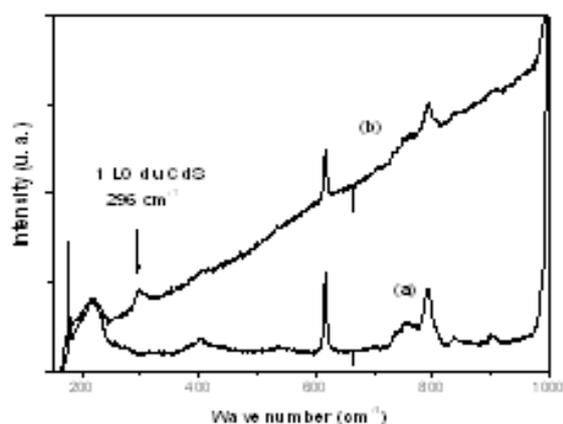


Fig. 3. Raman spectra, (a) Pure polystyrene and (b) CdS nanocrystals – polystyrene composite.

The absorption spectrum (Fig. 4) shows a shift towards shorter wavelengths of the absorption edge of CdS. To estimate the value in terms of energy of this shift, we compute the second derivative curve.

From figure 4, it can be seen that the absorption edge is 2.51 eV (494.02 nm), compared to the gap of the CdS bulk (2.50 eV [6]), the shift is thus 0.01 eV. Using the CdS equation [21]

$$E(R) = 2.50 + \frac{2.45}{R^2} - \frac{0.45}{R} \quad (2)$$

where $E(R)$ is the optical absorption edge (2.51 eV), and R the crystallite radius, we obtain 5.02 nm as an average crystallite radius. This value is near to the one obtained with Scherer's formula.

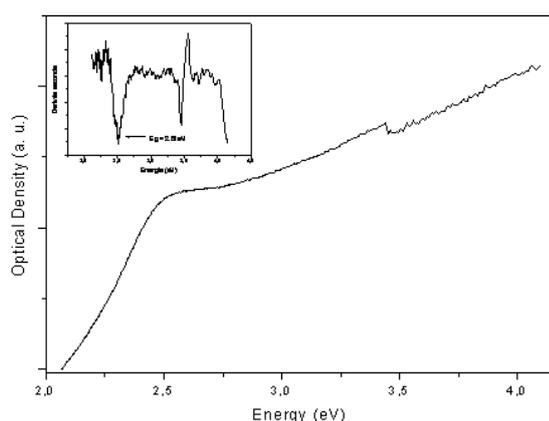


Fig. 4. Optical absorption of CdS nanocrystals embedded in polystyrene matrix, Inset second derivative curve.

The photoluminescence spectrum recorded at room temperature is shown in Fig. 5. A large band near absorption edge, centered at 2.50 eV, has been observed. This band is assigned to the band to band transition (annihilation of free exciton, FE) in CdS crystallites. We

notice the absence of the band emission from the sulfur vacant sites for the composite CdS nanocrystals – PS. The PS blocks surface states that affect the luminescence, which allows an increase in photoluminescence. This result is in good agreement with the work already done on the composite CdS – PS [22] and CdS nanocrystals embedded in silica glass by sol gel at low temperature [23] and colloidal route [24].

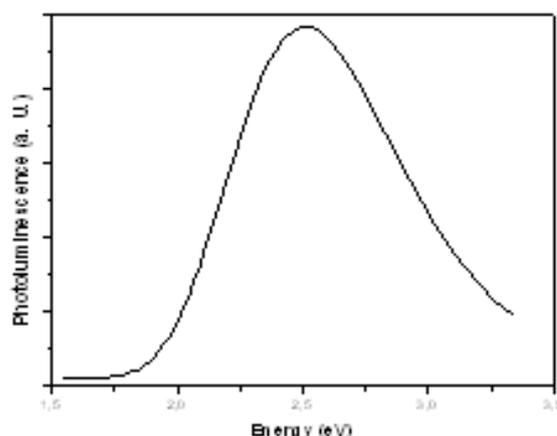


Fig. 5. Photoluminescence spectrum.

4. Conclusion

X-rays and Raman spectroscopy have confirmed the formation of the composite CdS nanocrystals – polystyrene. UV – visible UV visible Spectroscopy allows us to determine the size of crystallites of CdS embedded in polystyrene matrix. The average diameter has been found close to that determined by X-ray. Photoluminescence spectrum is constituted by one band situated at 2.50 eV. This band is attributed to the band to band transition.

References

- [1] A. Ekimov Journal of Luminescence **70**, 1 (1996).
- [2] B. Pejova, I. Grozdanov Materials Chemistry and Physics **90**, 35 (2005).
- [3] J. Mazher, S. Badwe, R. Sengar, D. Gupta, R. K. Pandey Physica E **16**, 209 (2003).
- [4] N. Murase, M. Gao Materials Letters **58**, 3898 (2004).
- [5] B. Pejova, A. Tanusevski, I. Grozdanov Journal of Solide State Chemistry **177**, 4785 (2004).
- [6] I. Mikulskas, E. Bernstein, J. C. Plenet, C. Bovier, R. Tomasiunas, V. Grivickas, J. V. Vitkus, J. Mugnier, J. Dumas; Mater. Sci. and Eng. B **69-70**, 418 (2000).
- [7] G. Khachatryan, K. Khachatryan, L. Stobinski, P. Toamsik, M. Fiedorowicz, H. M. Lin; J. Alloys Compd. (2009), doi:10.1016/j.jallcom.2009.03.011
- [8] K. S. Ramaiah, R. D. Pilkington, A. E. Hill, R. D. Tomlinson, A. K. Bhatnagar, Mater. Chem. Phys. **68**, 22 (2001).

- [9] O. Halimi, B. Boudine, M. Sebais, A. Chellouche, R. Mouras and A. Boudrioua *Materials Science and Engineering C* **23**, 1111 (2003)
- [10] B. Boudine, M. Sebais, O. Halimi, R. Mouras, A. Boudrioua, P. Bourson *Optical Materials* **25**, 373 (2004).
- [11] Y. Wang, X. Yao, M. Wang, F. Kong, J. He *Journal of Crystal Growth* **268**, 580 (2004).
- [12] Y. Wang, M. Wang, X. Yao, F. Kong, L. Zhang *Journal of Crystal Growth* **268**, 575 (2004).
- [13] L. Yang, Q. Shen, J. Zhou, K. Jiang *Materials Letters* **59**, 2889 (2005).
- [14] M. Mukherjee, N. Deshmukh, S. K. Kulkarni; *Applied Surface Science* **218**, 324 (2003).
- [15] Xinjian Cheng, Qiang Zhao, Yingkui Yang, Sie Chin Tjong, Robert K.Y. Li; *Journal of Colloid and Interface Science* **326** (2008) 121–128.
- [16] D. Sajinovi, Z. V. Saponji, N. Cvjeticanin, M. Marinovi Cincovi, J. M. Nedeljkovi; *Chemical Physics Letters* **329**, 168 (2000).
- [17] M. Feng, Y. Chen, L. Gu, N. He, J. Bai, Y. Lin, H. Zhan; *European Polymer Journal* **45**, 1058 (2009).
- [18] B. Boudine, M. Sebais, O. Halimi, H. Alliouche, A. Boudrioua, R. Mouras *Catalysis Today* **89**, 293 (2004).
- [19] P. Nandakumara, C. Vijayana, M. Rajalakshmi, Akhilesh K. Arora, Y.V.G.S. Murthy; *Physica E* **11**, 377 (2001).
- [20] Yu.P. Rakovich, M. Gerlach, J.F. Donegan, N. Gaponik, A.L. Rogach *Physica E* **26**, 28 (2005)
- [21] M. V. Artemyev, V. Sperling, U. Woggon; *J. of Appl. Phys.* **81**(10), 6975 (1997).
- [22] Dragana Sajinovic, Zoran V. Saponji, Nikola Cvjeticanin, Milena Marinovi Cincovi, Jovan M. Nedeljkovi; *Chemical Physics Letters* **329**, 168 (2000).
- [23] Rajh, M.I. Vucemilovic, N.M. Dimitrijevic, O.I. Micic, A.J. Nozik, *Chem. Phys. Lett.* **143**, 305 (1988).
- [24] M.I. Comor, J.M. Nedeljkovic, *J. Mater. Sci. Lett.* **18**, 1583 (1999).

*Corresponding author: hbloubna@yahoo.fr