Journal of Optoelectronics and Advanced Materials Vol. 3, No. 1, March 2001, p. 89 - 93

OPTICAL PROPERTIES OF POLYANILINE/CdS NANOCRYSTALS COMPOSITE FILM

V. Ghiordanescu, M. Sima, M. Nedelcu, M. Giubelan[a]

National Institute of Material Physics P.O. Box MG 7, Magurele, Bucharest, Romania
[a]"Politehnica" University of Bucharest, Romania

The optical spectra of CdS nanocrystals embedded in polyaniline matrix have been studied. The presence of surface states is revealed both in absorption and emission spectra. The polymer matrix determines a shift of the absorption edge of CdS nanocrystals, towards higher energies.

(Received August 3, 2000; accepted February 9, 2001)

Keywords: Cadmium sulfide, Nanocrystals, Polyaniline matrix

1. Introduction

The optical properties of nanocrystals have become the topic of both theoretical and experimental interest [1-6]. Although the structure of the bulk and nanocrystals is, up to a point, the same, a shift towards higher energy of the absorption edge can be observed when the particle dimension is decreasing. This behaviour can be explained by a molecular treatment i.e. each electronic band of the solid bulk is split into a series of discrete states [3].

An important characteristic of the nanocrystal systems is the very large value of the surface/volume ratio. As a consequence, the number of the surface states will increase [7,8]. If the excited electrons in the conduction band are captured on the surface states or other trap levels before exciton radiative recombination, the luminescence intensity due to electron-hole recombination decreases with decreasing nanocrystal size [7].

Nanocrystalline II-VI semiconductors were studied in different host media such as polymer [3,9-12], glasses [13], zeolites [14] or water [3].

In this paper we study a chemically prepared polyaniline/CdS nanocrystal composite, with the aim of observing, by optical methods, the interactions between the polyaniline matrix and the CdS nanoparticles.

2. Experimental

CdS particles were prepared at 278 K by bubbling hydrogen sulfide into a 80% formic acid aqueous solution containing 10^{-3} M $CdCl_2$ and, as a stabilizing agent, 10^{-3} M thioglycollic acid. The bubbling process was interrupted when our solution turned slightly yellowish; this colloidal solution was stable, without precipitation, for 12 hours. The colloids were reduced by evaporation to a redispersable powder.

Further, for a polyaniline/CdS nanoparticles composite preparation the CdS particles (0.16%) together with polyaniline (2.3%), ascorbic acid (1.15%) are dissolved into 80% formic acid. This solution of composite was spun-cast at 2000 rpm on a clean quartz glass. Similarly, a polyaniline film, without CdS particles was obtained.

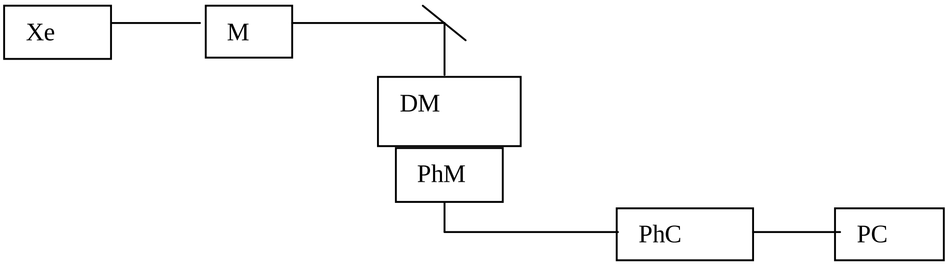

Fig. 1. Schematic drawing of the experimental arrangement for the emission measurements: Xe – xenon lamp; M – monochromator; DM – double - monochromator; PhM – photo - multiplier; PhC – photoncounting; PC – computer.

The nanoparticles samples obtained by evaporation of colloidal solution on a quartz glass and the composite film were characterized by absorption and emission spectroscopy at room and liquid nitrogen temperatures. Absorption spectra were recorded by a Specord UV-VIS spectrophotometer and the emission spectra, excited by a $\lambda = 250$ nm radiation, were obtained using an experimental set-up shown in Fig. 1. Here the detector was at 90^0 to the incident (exciting) light. The CdS particles dimension was estimated to be 14-16 nm from the micrograph (Fig. 2) obtained with a Philips EM 301 electron microscope.

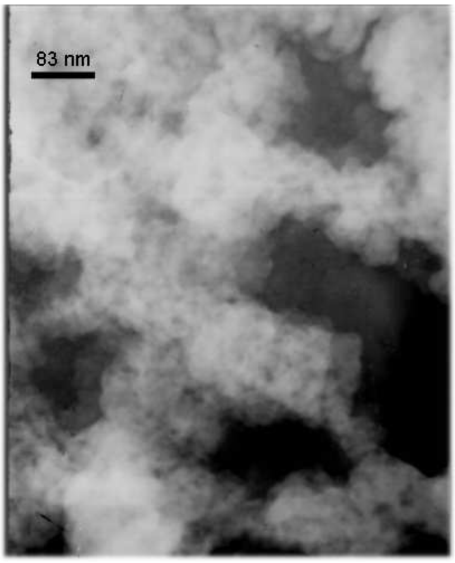

Fig. 2. Transmission electron micrograph of CdS nanoparticles.

3. Results and discussion

The polyaniline/CdS nanocrystals composite film, having a structure presented in Fig. 3, shows spectral characteristics both of pure polyaniline and CdS particles (Fig. 4).

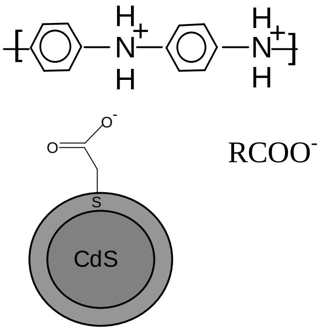

Fig. 3. Sketch of the structure of the CdS particle stabilized with thioglycollic acid and of the polyaniline matrix protonated with organic acids (formic and ascorbic).

Stilwell and Su-Moon Park [15] have reported that polyaniline matrix from the reduced state to the partially oxidized conducting form shows three absorption bands at 330, 440 and ~800 nm. The spectrum for the reduced form of polyaniline (leucoemeraldine) reveals a strong absorption band centered at 330 nm. In partially oxidized form of polyaniline (emeraldine) the spectrum shows an absorption band centered at 440 nm with an additional absorption at ~800 nm.

In our composite the prevalent polyaniline form is leucoemeraldine: the observed 334 nm strong absorption (Fig. 4a) is caused by the reduced form of polyaniline and the shoulder detected between 375 and 467 nm, together with the tail around 700-800 nm confirm the presence of a small concentration of protonated emeraldine.

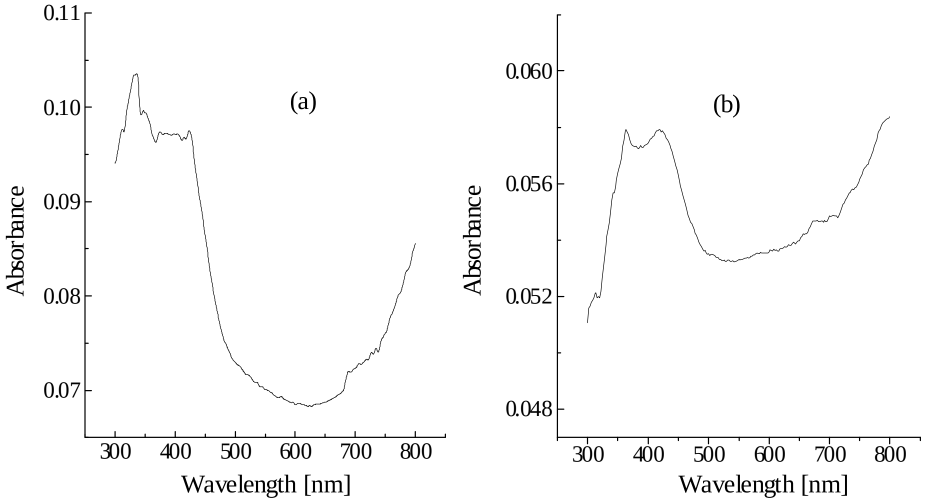

Fig. 4. Absorption spectra of the composite film polyaniline/CdS particles on a quartz glass substrate using as reference a quartz glass plate (a) or polyaniline film on quartz glass plate (b)

Beside the matrix absorption bands, the CdS nanocrystals absorptions are presented (Table 1). The 423 nm band corresponds to the direct band transition of CdS nanocrystals and it is displaced toward higher energies from that of the bulk (517 nm).

Table 1. Absorption and emission peaks position of the CdS sample in the polyaniline/CdS composite film.

Absorption peaks (nm)	Emission peaks (nm)
314	
347	
364	395
423	441
	466
500	503
	531
	563
580	610
	650
688	696
	763

UV bands located at 314, 347 and 364 nm are attributed to some excited states in the conduction CdS band. The absorption bands observed between 423 and 688 nm are due to the interactions of CdS particles with polymer matrix; some of them are reported elsewhere [16].

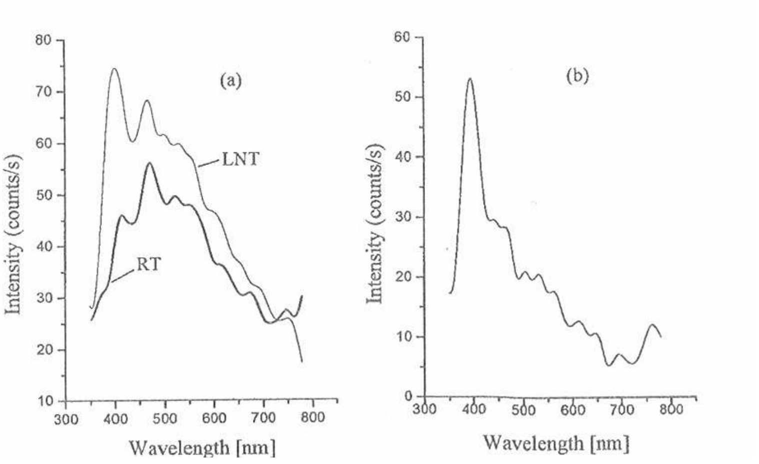

Fig. 5. (a) Emission spectra of the composite film polyaniline/CdS nanocrystals at room temperature (RT) and at the liquid nitrogen temperature (LNT). (b) Emission spectra of CdS nanoparticles at LNT, corrected for matrix contribution.

Fig. 5a shows the emission spectra of the composite polyaniline/CdS nanocrystals at LNT and RT. These emission spectra are more intense in the blue region at LNT. The intensity of the 375 and 415 nm emission bands increases at LNT while the intensity of the bands located at 470 nm and those ranging from 730 to 780 nm decreases compared with RT spectra. The emission bands at 470 nm and 730-780 nm correspond to the transitions from the surface levels to the valence band and will increase at high temperature. They are strongly influenced by transfer phenomena at semiconductor/ matrix interface.

The band edge spectra observed in II-VI compounds are consistent with the concept of bound exciton transition. Such spectra are variable in occurrence in a material with defects suggesting extrinsic origin. We observe some series in emission spectra (Fig. 5b); the blue margins of them correspond very well with absorption peaks (Table 1).

4. Conclusions

CdS particles and polyaniline/CdS nanocrystals composite film was chemically prepared in a reducing and highly protonated medium. It was observed both the quantum effects, resulted from the finite dimension of nanoparticle and the electronic interaction of CdS nanocrystals with polyaniline matrix; states due to the defects were identified in the emission spectrum that show a different behavior with temperature in comparison with CdS nanocrystal predicted states.

References

[1] C. R. Berry, Phys. Rev., **161**, 848 (1967).
[2] L. E. Brus, J. Phys. Chem., **90**, 2555 (1986).
[3] A. P. Alivisatos, A. L. Harris, N. J. Levinos, M. L. Steigerwald, L. E. Brus, J. Chem. Phys., **89,** 4001 (1988).
[4] A. Henglein, Chem. Rev., **89**, 1891 (1989).
[5] A. Hagfeldt, M. Grätzel, Chem. Rev., **95**, 49 (1995).
[6] A. P. Alivisatos, J. Phys. Chem., **100**, 13226 (1996).
[7] T. Arai, T. Yoshida, T. Ogawa, J. Appl. Phys., **26**, 396 (1987).
[8] I. Umezu,T. Ogawa,T. Arai, Japan J. Appl. Phys., **28**, 447 (1989).
[9] Y. Wang, A. Suna, W. Mahler, R. Kosowski, J. Chem. Phys., **87**, 7315 (1987).
[10] Y. Wang, A. Suna, J. McHugh, E. Helsinki, P. Lucas, R. D. Johnson, J. Chem. Phys., **92**, 8706 (1990).
[11] W. Mahler, Inorg. Chem., **435** (1988).
[12] S. Pethkar, R. C. Patil, J. A. Kher, K. Vijayamohanan, Thin Solid Films, **349**, 105 (1999).
[13] N. F. Borrelli, D. W. Hall, H. J. Holland, D. W. Smith, J. Appl. Phys., **61**, 5399 (1987).
[14] G. D. Stucky, J. E. MacDougall, Science, **247**, 669 (1990).
[15] D. E. Stilwell, Su-Moon Park, J. Electrochem. Soc., **136**, 427 (1989).
[16] K. K. Nada, S. N. Sarangi, S. Mohanty, S. N. Sahu, Thin Solid Films, **322**, 21 (1998).