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Thin films preparation, UV-vis Absorption and Photoluminescence property of CdSe nanoparticles dispersed in PMMA medium.

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Abstract

The content of this work deal with the preparation method, the effect of dimensional confinement and the influence of the nanoscale size on the optical properties of materials compared to those of bulk phase. CdSe nanoparticles have been prepared by mecanosynthese route then dispersed in PMMA medium to elaborate nanocomposite material CdSe/PMMA in thin film form by spin coating process the sample was characterized by X-ray diffraction, UV-vis optical absorption, and photoluminescence spectroscopy analyses. XRD patterns showed that CdSe nanoparticles have hexagonal unit cell structure. The UV-vis absorption spectrum of these dispersed NCs exhibit excitonic peaks at 2.67eV resulting from the electron-hole coupling transitions, attributed to optical gap energy and corresponding to a blue shift of the band edge equal to 0.93 eV due to nanosized CdSe .From UV-Vis absorption spectrum and by using the effective mass approximation model (EMA) the average particle size can be estimated to be 2.92 nm. Photoluminescence spectrum exhibits three emission peaks one at 538nm corresponding to band gap excitonic emission and another located at 581nm and at 699 nm,

Keywords: PMMA, Optical gap energy, EMA, NCs, quantum confinement, exciton.

1. Introduction

Semiconducting nanoparticles have attracted considerable interest due to their size dependent physical properties [1-3]. Particularly, CdSe NCs are considered as a reference material for investigation of fundamental physical properties of II-VI semiconductors NCs. CdSe of particle size in nanometer range have been paid more attention for their unique properties its make it an interesting material it was considered most promising candidate and performing materials in nanotechnology. That can be applied in optoelectronics and photonics devices such as laser diodes [4-5], frequency doublers, solar cells, electron–beam pumped lasers, optical devices [6] biological tags [7-85].The NCs deposited in thin films can be prepared by various deposition techniques like chemical vapor deposition (CVD), sputtering, electro deposition, vacuum evaporation, sol-gel process and colloidal solution.

2. Experimental.

2.1. Materials and Methods.

2.1.1. Thin film preparation of CdSe nanocrystals doped PMMA polymer matrix.

CdSe nanoparticles doped polymer polymethylmethacrylate (PMMA) was prepared by colloidal solution. A host solution was prepared by dissolving the polymer (PMMA) in tetrahydrofuran (THF) with a concentration of 0.02 g/ml. This solution was stirred at 50 °C for 2 hours. On another hand a guest solution was prepared with 0.153 g of mechanically crushed CdSe powder dispersed in 5 ml of THF. Then we take just the part of solution near the surface which containing only very small crystallites of CdSe and inject it in host solution. Finally the mixture

was stirred for several minutes and then allowed to stabilize. From this colloidal solution we prepared thin films of the composite material CdSe/PMMA deposited in a glass substrate using spin- coating process. The crystal structure

of the thin films was analyzed, using an X-ray diffractometer model D8 Advance, Bruker with Cu-Ka (λ=0.154 nm) irradiation. The absorption spectra were recorded on a (UV–vis)/NIR spectrophotometer (Perking Elmer, model Lambda 19) in the spectrum range from 200 to 1000 nm. The photoluminescence (PL) spectra were measured using a Q-switched Nd-YAG laser with fundamental emission at 1064 nm. To excite samples, we used the frequency tripled to355 nm. The measurements were performed at 77° K temperature of liquid nitrogen.

3 Result and discussion

3.1. Structural analysis.

PMMA matrix is by definition an amorphous polymer so transparent to X-rays. All the observed lines in the diagram are those related to the basic semiconductor CdSe. Diagram shows the lines located at diffraction angles in 2θ,: 23.54 ° 25.06 °, 26.71 ° and 41.58 ° corresponding respectively to the diffraction planes (100), (002), (101), (110) of the hexagonal structure (wurtzite) of CdSe assigned by a standard JCPDS data base file n° 08-0459. The shape of the spectrum can be inferred that the CdSe crystallites have a random orientation with a slight preferential orientation along the (100) plane parallel to the substrate surface. (Fig).

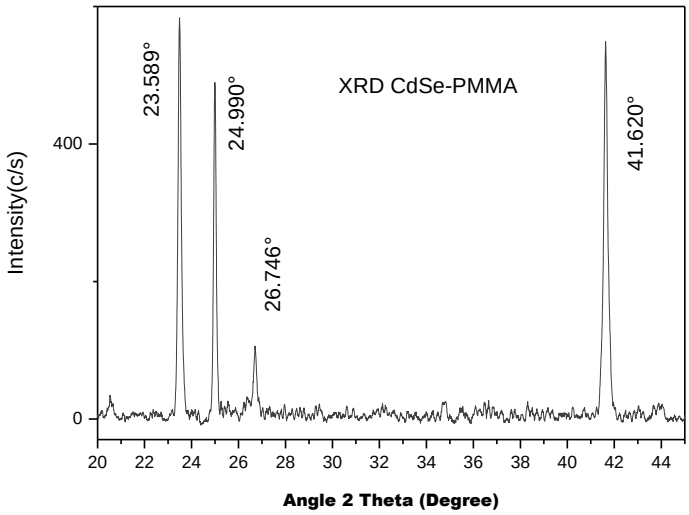

Fig.1. XRD of thin film of CdSe/PMMA Composite.

3.2. Optical analysis

3.2.1. Measurement of the optical absorption of CdSe / PMMA composite

From the shape and profile of the absorption spectrum of the composite CdSe / PMMA, and more rigors in determining the optical gap, corresponding to the maximum absorption, the use of the second derivative is most appropriate. The optical gap was estimated around 2.67 eV (Fig.2). This shift of the gap to larger energy commonly called blue shift is mainly caused by the low dimensionality of CdSe crystallites, which induces a significant effect on their optical properties due to quantum confinement in these nanostructures.

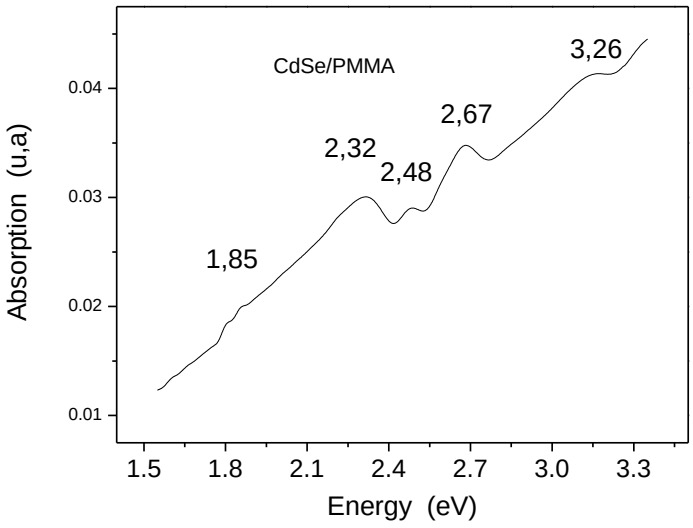

Fig.2 .UV-vis absorption Spectrum. CdSe nanoparticles

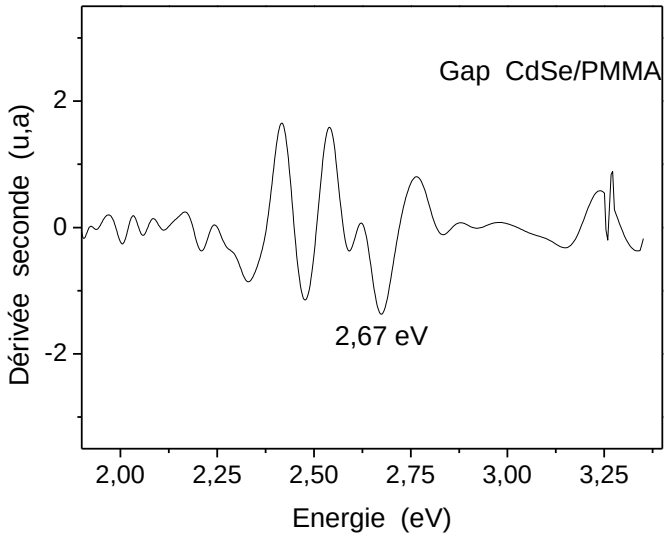

Fig.3. Optical gap

The profile of the absorption spectrum of the CdSe / PMMA composite is determined by transitions between energy levels of the electrons and holes respectively of energy levels (LUMO) and (HOMO). The absorption spectrum (fig.2) shows a shift of the absorption edge equal to 0.93 eV towards high energies relative to that of bulk CdSe[13]; hence we can conclude that there is a important decrease in crystallite sizes of CdSe; compared to bulk material and created a quantum confinement effect ;on the other hand in this spectrum we can observe and define the various transitions, which are represented by three positions related to exciton transitions with energies of 2.32, 2.48, 2.67eV, respectively.

The first peak at 2.32 eV corresponds to the first transition the most intense $1S_{3/2}$ -- $1S_e$

The second peak at 2.47 eV to the transition $2S_{3/2}$ -- $1S_e$. Let us note that the relative positions of these transitions exchange with the size of nanocrystallites. We summarize in the following table (tab.1) the different transitions of the CdSe / PMMA composite, we compare our results to the work of Ekimov et al on CdSe nanocrystals size 2.6 nm doped glass [9].

Peak	Transition	CdSe//PMMA Position (eV)	Ekimov et al CdSe doped glass	Intensity
Peak N°1	$1S_{3/2}$ -- $1S_e$	2.31	2.25	strong
Peak N°2	$2S_{3/2}$ -- $1S_e$	2.48	2.38	weak
Peak N°3	$1P_{3/2}$ – $1P_e$	2.67	2.75	strong
Peak N°3	$2S_{3/2}$ -- $2S_e$	3.26	3.2	average

Tab.1.The main transitions of the CdSe / PMMA nanocomposite.

This comparison strongly consolidates our results and confirms the nanometer size of CdSe. Using the model of the effective mass approximation (Kayanuma and Brus model) [10] we can estimate the crystallite size of CdSe in PMMA].From resolving the following Brus's formula [11],the grain sizes of the prepared samples have been calculated and estimated to 2.92 nm.. According to the model (EMA), where the size of the exciton is smaller than the Bohr radius (R_B=5.5nm), electrons and holes are strongly confined in the crystallite. This result is in good agreement with those reported by Murray et al [12] and Miroslav Šimurda et al [13].

$$E^* = E_g + \left(\frac{\hbar^2}{2R^2}\frac{\pi^2}{m_0}\right)\left(\frac{1}{m^*_e} + \frac{1}{m^*_h}\right) - \frac{}{\varepsilon_0}\frac{1.8e^2}{4\pi\varepsilon R}$$

Where $E^*(R)$ the optical band gap energy and Eg is the bulk band gap equal to 1.74 eV [13] expressed in eV. _ is Plank's constant, R is the particle radius, m_e*is the electron effective mass, m_h*= is the hole effective mass, m_0 is free electron mass, e is the charge on the electron, ε is the relative permittivity, and ε_0 is the permittivity of free space. Due to the relatively small effective masses for CdSe (m_e* = 0.13, m_h*= 0.45), [13]. The average radius of NCs inside the thin film is estimated to be 2.92 nm.

3.2.2. Measurement of photoluminescence of the CdSe / PMMA composite.

The photoluminescence of the CdSe / PMMA composite achieved in the range of spectral from 400 to 700 nm under excitation of 355 nm from pulsed laser Nd: YAG with tripled frequency this excitation energy is much higher than that of the gap. This allows for the contribution to emission any whereby the size distribution of the NCs CdSe / PMMA composite. The luminescence spectrum is obtained at 77 K (liquid nitrogen temperature) . After a Gaussian deconvolution, we see the emergence of three emission bands located around de538 nm, 581nm and at 699 nm. The first peak at 538 nm (2.30 eV) is the recombination of electron-hole of the first transition $1S_{3/2}$ -- $1S_e$ with energy equal to 2.32 eV. The second peak of lower intensity 581.50 nm (2.13 eV) corresponding to the electron-hole recombination of the second transition $2S_{3/2}$ -- $1S_e$ and the third peak wider around 690 nm (1.79 eV) corresponds to the electron-hole recombination transition $2S_{3/2}$ -- $2S_e$ near the optical gap of CdSe bulk. We notice the absence of the transition corresponding to the recombination $1P_{3/2}$ – $1P_e$ no doubt that this is a non-radiative recombination.

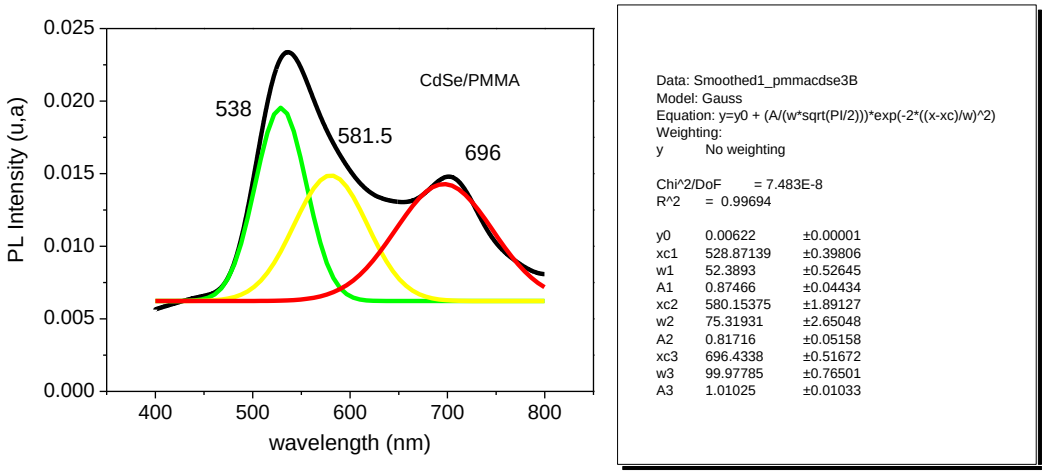

Fig 3.Photoluminescence spectrum of thin film of CdSe /PMMA nanoparticles (λ_{exc}=355 nm).

4. Conclusion.

The average radius of NCs inside the thin film is estimated to be 2.92 nm. Such result shows that the decreasing of the crystallites size leads to an enhancement of the optical gap energy. By comparing the CdSe NCs average size to the Bohr radius of the exciton which is about r_B = 5.5 nm, we obtain R < rB corresponding to a strong confinement regime. With a relatively simple and with low cost method of preparing we could carry out a nanocomposite material with best linear optical properties (absorption and emission) with an enlargement of the optical gap. By controlling the crystallites size of these materials we can cover a wide range of optical application. Among the inorganic semiconductor II-VI CdSe nanostructure may be a very good candidate for fully optical applications.

Reference

[1] C. Murray, C. Kagan, M. Bawendi, Annu. Rev. Mater. Sci. **30**, 546 (2000),

[2] A. Efros, Rosen, M. Annu. Rev. Mater. Sci. **30**, 475 (2000).

[3] [8] U. Woggon, Optical Properties of Semiconductor Quantum Dots; Springer: New York, (1997).

[4] S. Nakamura, in: G.B. String fellow, M.G. Craford (Eds.), High Brightness Light Emitting Diodes,

Academic Press, New York, **48,** 391 (1997).

[5] M. Yano, M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori, T. Sasaki. Diamond and Related Materials, **9**, 512 (2000).

[6] L. Brus, Appl. Phys. A: Mater. Sci. Process. **53**, 465 (1991).

[7] C. Nadrian. Seeman and Angela, M Belcher. PNAS, **99**, 6451 (2002).

[8] H. Mattoussi, J. Mauro, E. Goldman, G. Anderson, V. Sundar, F. Mikulec, M. Bawendi, J. Am. Chem.Soc. **122**, 12142 (2000),

[9] Ekimov *et al.* J. Opt. Soc. Am. B/Vol. 10, No. 1/January 1993

[10] Landolt-Börnstein, Handbook of Physics, vol. 17b, Springer, Berlin, (1982);

[11] Kayanuma.Y, Phys .Rev B **38**, 9797 (1988).

[12] [9] C. B. Murray, D. J. Norris,and M. G. Bawendi. J. Am.Chem. Soc. **115**, 8706 (1993),

[13] M. Simurda, P. Nemec, P. Formanek, I. Nemec,Y. Nemcova, P. Maly, Thin Solid Films

503, 64 (2006).

[14] Handbook, Physico-Chemical Properties of Semiconductor Compounds, Nauka, Moscow, 1979.